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The Reactions Between Atomic Deuterium and the Saturated Aliphatic Hydrocarbons

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The exchange reactions between atomic deuterium and methane, ethane, propane and butane have been studied in the range of temperatures, 0–300°C, in each case until significant amounts of exchange have been obtained. The extent of deuterization and the nature of the fragments produced have been examined by fractionation analysis and determination of the thermal conductivities of the fractions. From the temperatures at which the several interactions occur, approximate values for the activation energies of the individual processes have been deduced and these have been shown to conform with the mechanisms of reaction formulated. It has been indicated that deuterization of alkyl radicals in presence of atomic deuterium is a more rapid process than the deuterization of the saturated hydrocarbons. From the activation energies obtained, values for the bond energies $CH_3-H=108$ kcal. and $CH_3-CH_3=97.6$ kcal. have been deduced. The discrepancies between these and other values have been emphasized. The uncertainty of the value of the steric factor in the activation energy calculations has been indicated and its influence on the results derived has been exhibited.

AS a supplement to our earlier* work on the interaction of deuterium and methane in the presence of mercury vapor and illuminated by the resonance radiation of mercury, $\lambda=2537$A, we have studied the interaction of atomic deuterium, produced in a modified Wood's hydrogen discharge tube,[3] and the aliphatic hydrocarbons methane, ethane, propane and butane. The technique in general follows that described by Bonhoeffer and Boehm[4] and applied more particularly to hydrocarbons by Bonhoeffer and Harteck,[5] and by von Wartenberg and Schultze.[5a] These workers used water vapor in the hydrogen to poison the vessel walls against recombination of atomic hydrogen, but as Chadwell and Titani[6] found that hydrocarbons were oxidized to carbon dioxide to 50–80 percent under "wet" conditions, we aimed to employ, as far as possible, dry gases. Smallwood[7] found that concentrated sulphuric acid acts as a good poison for the hydrogen atom wall recombination and we have followed this procedure.

In addition to the work of Bonhoeffer and Harteck, experiments by Geib and Harteck[8] have indicated that methane and atomic hydrogen do not interact at temperatures up to 170°C. More recent extension of this work by Geib and Steacie[9] and by Steacie and Phillips[10] to the interaction of deuterium atoms with methane and ethane confirmed this view and have led to an activation energy for the reaction $CH_4+D=CH_3D+H$ of 11 kcal. Very little exchange was

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* This issue, following paper.
[3] R. W. Wood, Phil. Mag. **42**, 729 (1921); **44**, 538 (1922).
[4] Bonhoeffer and Boehm, Zeits. f. physik. Chemie **119**, 385 (1926).
[5] Bonhoeffer and Harteck, Zeits. f. physik. Chemie **139A**, 64 (1938).
[5a] von Wartenberg and Schultze, Zeits. f. physik. Chemie **2B**, 1 (1929).
[6] Chadwell and Titani, J. Am. Chem. Soc. **55**, 1363 (1933).
[7] Smallwood, J. Am. Chem. Soc. **56**, 1542 (1934).
[8] Geib and Harteck, Zeits. f. physik. Chemie **170A**, 3 (1934).
[9] Geib and Steacie, Zeits. f. physik. Chemie **B29**, 215 (1935).
[10] Steacie and Phillips, J. Chem. Phys. **4**, 461 (1936).

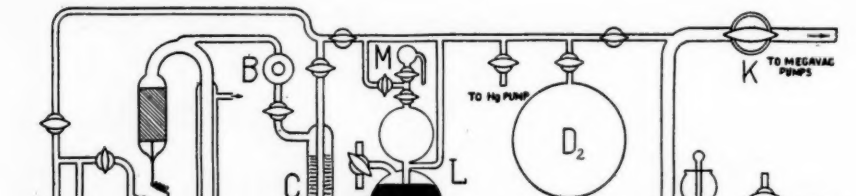

FIG. 1.

secured in the latter work but, with ethane, the production of deuteroethanes by exchange with atomic deuterium at 25°C was claimed. Our own work has been extended to temperatures where appreciable exchange occurs with methane and we have made a more extensive examination of the interactions with the higher hydrocarbons than hitherto, with new and important results.

EXPERIMENTAL DETAILS

Materials used

The preparation and purification of the methane, ethane, propane, deuterium and hydrogen used in this work have already been described in previous reports from this laboratory.[11] The butane used was prepared by repeated fractionation of tank butane. As used it may have contained a little isobutane and butylene.

Apparatus and experimental method

The apparatus is shown in outline in Fig. 1. Deuterium or hydrogen was introduced to the discharge tube *A* through an adjustable valve *B*, through a liquid-air trap *C* from a reservoir *D* automatically kept at constant pressure. The discharge tube was water-cooled and poisoned by allowing to stand under vacuum in an atmosphere of H_2SO_4 vapor when not in use. This sufficed to insure adequate atom concentrations even under dry conditions. The atom stream passed through a 3 mm orifice *E* to the water-cooled connecting tube between discharge tube and reaction vessel *F*.

The hydrocarbon was introduced into the reaction vessel from flask *N* through a solid CO_2 trap *G* packed with copper granules. The two gas streams met and intermixed at two jets located centrally in the spherical reaction vessel, 500 cc in volume. The gas pressures were measured on an oil manometer *H* (Apiezon vacuum oil; density $=0.86$ at 26°C). The exit gases passed through a mercury cut-off *I* and thence to a special low temperature trap *J* in which the gaseous hydrocarbons were frozen. Test showed that 60–90 percent of the methane was recoverable, thus depending on the prevailing partial pressure. The residual hydrogen isotopes passed on to the pumping system, two megovac pumps in parallel.

The low temperature in trap *J* was attained by evaporating liquid air located around the trap and in two co-axial Dewar vessels, the outer one containing liquid air at atmospheric pressure. The pressure over the liquid air in the inner

[11] Morikawa, Benedict and Taylor, J. Am. Chem. Soc. **58**, 1445 (1936) and a forthcoming paper by Morikawa, Trenner and Taylor in J. Am. Chem. Soc.

vessel was 4 mm corresponding to a temperature of $\sim -230°C$.

Rates of gas flow were calibrated by measures of the volumes actually consumed from the respective reservoirs during a run. The discharge tube was operated from a 6000 volt 2 kva transformer, the tube current being read directly from an a.c. milliammeter in the tube circuit. A variable resistance in the primary circuit served as a current control.

The D (or H) atom concentration was determined by measuring the extent of exchange in the reaction $H+D_2$, the exit gases being analyzed by means of a Farkas thermal conductivity gauge.[12] We employed in our calculations of the atom concentrations from the reaction $H+D_2=HD+D$, the data of A. and L. Farkas,[13] $E=6.55$ kcal., $k_{299}=4.9\times10^5$ liter mole sec.; steric factor, $s=0.1$. A blank run, $W1$, with D_2 alone showed a negligible amount of light hydrogen so that reaction with manometer oil, or other light hydrogen sources, is unimportant. The absence of hydrocarbon in the discharge tube was shown by spectroscopic observation of the light emitted in the discharge and by calculation of the back diffusion against a linear velocity of flow reaching 2400 cm per sec. through the orifice E.

The temperature of the reaction vessel when hot was attained by surrounding the vessel with an electric furnace. All temperatures cited are mean temperatures from several thermometers located at different places within the furnace. The temperature control was manual.

Operating conditions

Normal operating conditions were: Total pressure, 0.5 mm Hg; deuterium flow rate, 600 cc per hour at N.T.P.; hydrocarbon flow rate, 100 cc per hour S.T.P.; contact time, 1.8 sec.; arc current, 350 ma; D atom concentration, 10 to 20 percent; temperature of trap J, $\sim -230°C$; duration of run, ~ 1 hour. The discharge tube was always operated for 0.5 hour before the hydrocarbon was introduced; the D_2 hydrocarbon ratio was adjusted by pressure.

After about 100 cc hydrocarbon were passed, the cut-off I was raised and the low temperature trap J was thoroughly evacuated for 10–15 minutes and the trap finally isolated by closing the main stopcock K to the pumps. The liquid air in the inner Dewar vessel was then raised to normal temperature by raising the pressure over it to atmospheric pressure. The methane present in the trap now showed a measurable vapor pressure and was removed by a Töpler pump L to a sampling tube M. After methane removal, the trap was raised in temperature to $-78°C$ and the next higher fraction was collected in a sampling tube M by means of the Töpler pump. Finally, the trap temperature was raised to room temperatures and any residual vapors pumped off with the Töpler pump and put into a sampling tube for future analysis. These latter samples throughout the investigation contained only traces, i.e., *less* than 0.5 percent, of higher hydrocarbons and water. No carbon dioxide was found.

The details of the fractionation purification procedure for these samples will be described elsewhere,[14] as it has general applicability. The methane fraction was passed over copper oxide at 270°C to remove traces of hydrogen isotopes. This does not cause any exchange.[11] It was fractionated once more from liquid air to remove traces of higher hydrocarbons. The total volume thus received was measured and then analyzed for exchange by means of a thermal conductivity gauge developed by one of us (N.R.T.)[15]

The fractions containing higher hydrocarbons received the following treatment. Residual methane was removed by a Töpler pump at liquid-air temperatures and the amount thus recovered was measured. The residue was hydrogenated with light hydrogen on catalytic copper at 60°C to remove possible traces of olefines.

These latter never exceeded 1 percent even when estimated before or after separation of methane. The excess hydrogen was removed on copper oxide at 300°C and by evacuation at liquid-air temperature. In the ethane runs the residual ethane was fractionated into several samples, the first and last samples were rejected and the middle samples collected for exchange analysis. In the propane experiments this final fractionation was conducted to give an ethane-rich fraction containing small amounts of propane

[12] We are indebted to Mr. E. A. Smith of this laboratory for these analyses.

[13] A. and L. Farkas, Proc. Roy. Soc. **152**, 147 (1935).

[14] Morikawa and Trenner, J. Am. Chem. Soc. forthcoming paper.

[15] N. R. Trenner, J. Chem. Phys. forthcoming paper.

and a propane-rich fraction from which a middle cut gave a sample for exchange analyses.

In order to avoid possible errors in the thermal exchange analyses of the hydrocarbons due to the presence of other hydrocarbons as a result of improper fractionation the several middle cuts were always thermally analyzed and, unless all cuts agreed, the results were rejected and the whole subjected to refractionation and thermal analysis until such agreement was obtained, when pure gas fractions were obviously being studied. Very few such refractionations were required, proving the precision of our separation methods. Further, the composition of the ethane sample was ascertained by reaction with hydrogen on a nickel catalyst at 300°C to yield methane whence the value of n in C_nH_{2n+2} could be determined. In the case of butane, the higher hydrocarbons were separated into ethane, propane and butane cuts by repeated refractionations and samples of middle cuts reserved for exchange analysis.

A special analysis of the ethanes from runs *W*15, 16 and 19 was made. The ethane fractions from each were combined and carefully refractionated. The C_2 fraction (17.4 cc) was divided into two portions. On one, a hydrogenating decomposition to methane on nickel gave a formula $C_2H_{5.6}$ for the fraction. The second portion was hydrogenated on copper with H_2 to convert olefines to saturated hydrocarbons. 8 percent of the whole fraction was thus found to be C_2H_4. The excess hydrogen was then removed by evacuation at liquid-air temperatures with the Töpler pump and reserved for exchange analysis. The deuteroethane was freed from traces of hydrogen by copper oxide and also reserved for exchange analysis. Less than 1 percent deuterium was found in the hydrogen thus also confirming the absence of large amounts of olefines since these exchange with hydrogen over copper at 65°C.[16] As shown in Table I, the ethanes analyzed 50.8 percent C−D bonds. We shall deal later with the significance of this result.

[16] Morikawa, Trenner and Taylor, J. Am. Chem. Soc. forthcoming paper.

TABLE I. *Results of D + hydrocarbon reactions.*

Run No.	Hydrocarbon Used	Temp.	Press. Ratio	Hydrocarbons Recovered					Hydrocarbon	Exchange		
				Methane		Ethane	Propane	Butane		in % = $\frac{C-D}{C-H+C-D}\frac{100}{}$		
	cc (1 atmos. & 25°C)	°C	D_2 : HC mm of oil[d]	cc	% Recov.	cc	cc	cc	Decomposed in Percent	CH_4	C_2H_6	C_2H_5
*W*2	CH_4+H 219	28	5 : 0.25 mm H_2SO_4	153	70	0	0	0	—	—	—	—
*W*3	CH_4+D 73	28.4	4 : 0.2 mm H_2SO_4	62	85	—	—	—	—	0 (by infrared)	—	—
*W*6	CH_4+D 90	26.3	5 : 0.45	85	94	—	—	—	—	0	—	—
*W*9	CH_4+D 83.4	103	6.3 : 0.4	76.5	92	—	—	—	—	0	—	—
*W*11	CH_4+D 93.8	165	6.1 : 0.8	70	74.6	—	—	—	—	0	—	—
*W*12	CH_4+D 81.0	208	6.0 : 0.4	70	86.4	—	—	—	—	0	—	—
*W*17[c]	CH_4+D 79.5	310	6.0 : 0.5	63.7	80.2	—	—	—	—	9.6	—	—
*W*7	C_2H_6+D 131 (calc.)	27.3	4.5 : 0.75	16.9	60 (assumed)	117	—	—	10.6	53.5	0	—
*W*8	C_2H_6+D 94 (calc.)	103	6.8 : 0.40	27.0	60 (assumed)	71.2	—	—	24.2	46.5	0	—
*W*10	C_2H_6+D 98	166	5.7 : 0.8	21.0	55.0	78.9	—	—	19.5	35.0	7.0	—
*W*13	C_2H_6+D 97.3	208	6.0 : 0.5	16.0	52.3	82.0	—	—	15.7	53.0	13.6	—
*W*14[c]	C_2H_6+D 86.4	25	6.0 : 0.5	24.7	81.2	68.5	—	—	20.7 (D conc.	63.0	0	—
*W*18[c]	C_2H_6+D 90.8	110	6.0 : 0.5	26.8	68.0	71.1	—	—	21.6 (abnormal	50.7	3.6	—
*W*20[c]	C_2H_6+D 92.2	192	6.0 : 0.5	12.4	49.2	79.5	—	—	13.8	47.5	9.1	—
*W*15[c]	C_3H_8+D 99.5	24.7	6.0 : 0.5	4.3	71.7	≥0.8 } 12.5	97.0		2.4	90.5	} 50.8	0
*W*16[c]	C_3H_8+D 89.3	109	6.0 : 0.5	11.1	69.6	≥6.3 }	79.8	—	10.6	60.0		0
*W*19[c]	C_4H_{10}+D 93.3	110	6.0 : 0.5	10.1	—	4.9	3.2	83.0	11.0	72.5		0
*W*1[a]	D alone	26.5	3.5 mm H_2SO_4	—	—	—	—	—	—	—	—	—
*W*5[b]	D_2+H	26.5	H_2 : D_2 4.9 : 2.6 = 7.5	—	—	—	—	—	—	—	—	—

Olefines absent to ≪ 1% in all runs

[a] Percent D_2 used = 98.5 percent; percent D_2 recovered 97.5 percent; ∴ exchange negligible.
[b] In *W*5 the H atom concentrated calculated to be 9.4 percent giving 34 mole percent of HD in a contact time of 1.8 sec. in a system of 39 atom percent D and 61 atom percent H at a total pressure of 0.49 mm Hg. Temperature = 26°C.
[c] Experiments marked *c* were run with an initial D atom concentrate of about 20 percent, the others with about 9–10 percent D atom concentrate.
[d] Values of pressure are given in mm of oil except where otherwise indicated.

The efficiency of the fractionation procedure can be ascertained from this last example. The amount of ethane recovered from *W*19 is more accurately known because of favorable fractionation conditions, the propane content was small, and amounted to 4.9 cc. The combined C_2 fraction in *W*15, 16 and 19 was 17.4 cc or 17.4−4.9=12.5 cc from *W*15 and 16. A direct single fractionation in *W*15 and 16 separately gave a total of 7.1 cc. The ethane total in *W*15 and 16 obtained by the subtraction process is smaller than the methane recovered in these runs, 15.4 cc, which is only 70 percent of the total methane formed in the reaction.

Experimental results

Although our general operating conditions were rather similar in every respect to those employed by Bonhoeffer and Harteck[5] in their investigations of the reactions induced in the aliphatic hydrocarbons by hydrogen atoms, with the exception that dried gases were employed by us while the former workers used wet hydrogen, we did not observe the luminescence which they reported. We are somewhat at a loss to account for this but suggest that it may be associated with the use of wet hydrogen which Chadwell and Titani[6] found, as previously indicated, always resulted in considerable oxidation to carbon dioxide of the alkyl halides studied by them. We feel that the fact that the spectrum associated with this luminescence was, to quote from Bonhoeffer and Harteck's paper, "the spectrum of burning hydrocarbons" is significant when considered in the light of Chadwell and Titani's results and may be associated with the oxidation processes of the type studied by Geib and Harteck.[8] We did not find appreciable amounts of unsaturated products as reported by these former workers although carefully sought. We shall discuss reasons for this later.

In comparing our results on all hydrocarbons *above methane* with those of Bonhoeffer and Harteck it should be borne in mind that the temperature in their reaction system was quite high, estimated to be 300° at the center of the reaction zone, while in our case measurement within the reaction region showed only a few degrees rise at room temperatures. This, as will be indicated later, somewhat changes the nature

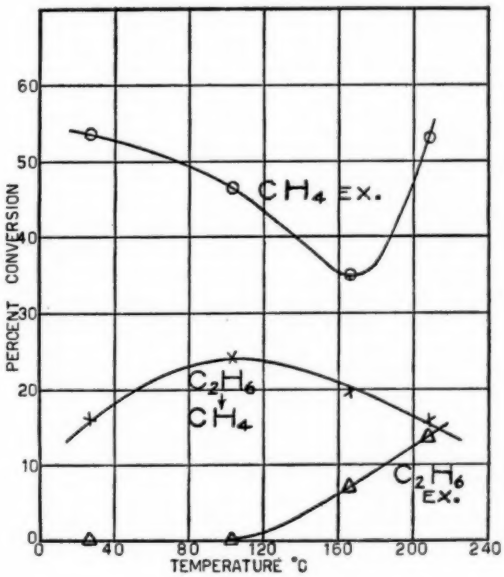

FIG. 2.

of the reactions involved and may account for some of the differences observed. In the case of methane no such temperature rise occurred in Bonhoeffer and Harteck's experiments.

The results are summarized in Table I. Two D atom concentrations were used, 10 and 20 percent, the latter indicated by a letter *c*.

The methane reaction

No exchange occurred between 25 and 208°C. At 310°, a definite exchange of 10 percent occurred. Under the experimental conditions this corresponds to a *minimum* activation energy of 15.6 kcal., when the relative rates of $H+D_2$ and $D+CH_4$ are compared. The minimum value arises from the fact that the mean rate of HD formation over a period of time was measured, not the initial rate which is certainly greater. A calculation based on the absolute rate of reaction at 310°C gives a value of $E=18$ kcal. which we regard as an *upper* limit. The calculation employs the kinetic expression $v=sZe^{-E/RT}$. For Z we write

$$10^{28.44}C_1C_2(\sigma_1+\sigma_2)^2\left(\frac{T(M_1+M_2)}{M_1M_2}\right)^{\frac{1}{2}},$$

where $\sigma_D=2.1\times10^{-8}$, $\sigma_{CH_4}=3.8\times10^{-8}$, $T=583°K$ and $C=P/T\,62.35\times10^{-3}$. The total working pressure was 0.41 mm Hg composed of 6 parts D_2 to 1 part of hydrocarbon or 0.07 mm CH_4 and

0.034 mm D on the basis of a 10 percent D atom concentration. This yields for the concentration terms $C_D = 0.94 \times 10^{-9}$ mole/cc and $C_{CH_4} = 1.93 \times 10^{-9}$ mole/cc. This yields a value for $Z = 3.15 \times 10^{-3}$ mole/cc/sec., whence, with a steric factor $s = 0.1$, we deduce from $v = 3.22 \times 10^{-11}$ mole/cc/sec. a value for $E = 18.7$ kcal. If the D atom concentration were as low as 5 percent, the corresponding E would be 17.9 kcal. Additional uncertainties in this calculation are the steric factor $s = 0.1$ and the assumption that the rate of CH_3 production is one-third the rate of C–D bond formation owing to the rapid exchange occurring with CH_3 radicals as revealed in subsequent data.

Both the upper and lower values for E are, however, definitely greater than the value $E = 11.5$ kcal. reached by Steacie and Phillips from the mercury photosensitized reaction and this is true also for the corresponding data of Morikawa, Benedict and Taylor,[17] indicating that this quantity cannot be determined readily by photosensitization experiments.

The ethane reaction

Decomposition by atomic deuterium to form methane occurs from 27° upwards but ethane exchange does not measurably occur under our conditions below 100°. This latter result differs sharply from that recorded by Steacie and Phillips. Our observation is strengthened by the similar absence of exchanged propane and butane in Expts. *W*15, 16 and 19 at temperatures from 25° to 110°C. Above 100°, we find increasing ethane exchange with increasing temperature. Typical results are given in Fig. 2.

In respect to the methane formed we direct attention especially to the high D content of the product. In one experiment *W*14, this reaches the high value of 63 percent, which, upon a basis of primary split to yield $CH_3 + CH_3D$, requires that the methyl radical be completely exchanged to CD_3 before stabilization as a deuteromethane molecule CD_4. In all the other ethane experiments, while not so complete as in *W*14, extensive D substitution in the methane has occurred. This result is confirmed by the extensive C–D bond content of the composite ethanes from propane and butane.

[17] Morikawa, Benedict and Taylor, J. Chem. Phys. **5**, 212 (1937).

Calculations from the absolute rates of reaction analogous to that outlined in the case of methane give the following activation energies. For the C–C bond split in ethane to yield methane at 26°C we calculate

$$C_2H_6 + D \xrightarrow{299°K} CH_3 + CH_3D; \qquad E = 7.2 \text{ kcal. } (s = 0.1).$$

For the exchange reaction at 110°C we obtain

$$C_2H_6 + D \xrightarrow{383°K} C_2H_xD_y + H; \qquad E = 11.4 \text{ kcal. } (s = 0.1).$$

This latter value is greater than that calculated by Steacie and Phillips, $E = 6.3$ kcal., based on reaction at room temperature.

The propane and butane reactions

The striking features of these reactions in addition to the deuterium content of the ethanes produced are the relatively small decomposition of these hydrocarbons and, again, the high degree of deutero-substitution of the methanes produced. Comment has already been made on the excess of methane formed over ethane from propane and over propane from butane.

Comparison of the total consumption of D atoms actually used in reaction at low temperatures (110°C) can be estimated from the data presented in runs *W*16, 18 and 19, Table I. Rounding off decimals as unimportant for our present purposes and bearing in mind that exchanges of type $CH_3 + D \rightarrow CH_2D + H$ do not remove H atoms we find 44 cc of methane formed in *W*18 which obviously involves the consumption of 44 cc of D atoms. Since in all these cases 60 cc of D atoms were engaged we find 16 cc of these D atoms are unused by the ethane and must recombine on the walls. In the case of propane, *W*16, the figures are 24 cc of split hydrocarbon products equivalent to 24 cc of D atoms used or 36 cc of D atoms unused. Similarly in the case of butane, *W*19, a total of 24 cc of split products were formed which corresponds to 36 cc of D atoms unused as in the case of propane. This relatively smaller reactivity of the higher hydrocarbons over that displayed by ethane is, we feel, due to a kind of greater steric hindrance in the former cases to the approach of a D atom possessed by virtue of their "cork screw" con-

figuration. This steric hindrance effect is greater in its reducing effect upon the reactivity than the increasing influence by virtue of the somewhat similar C−C and C−H bond strengths which exist in these higher hydrocarbons. In any case we cannot see the need nor evidence for the introduction of the Bonhoeffer and Harteck postulation of a "catalytic" recombination effect of the higher hydrocarbon molecules by means of a hydrogenation-dehydrogenation mechanism for the explanation of our results. About 50 percent of the introduced D atoms are on the average consumed in splitting reactions, the remainder cleaning up on the walls etc., diffusion to the walls being not excessively slow at our low pressures for fast moving H atoms in the narrow connecting tubing encountered on leaving the reaction vessel. Subsequent more exact measurements of the relative temperature coefficients involved may decide the adequacy of our steric postulate to account for the smaller reactivity of propane and butane over the existence of real activation energy differences which our present data do not seem to show.

Discussion of Results

Reaction mechanisms

The evidence available in the interaction of atomic deuterium with methane which only occurs measurably in the neighborhood of 300°C in the present work does not permit a decision between the two alternative processes (a) $CH_4+D=CH_3D+H$ and (b) $CH_4+D=CH_3+HD$ followed by reaction of the methyl radical. However, we know from our earlier work[17] and the present work with ethane that methyl radicals readily react with molecular hydrogen at temperatures above about 165°C. For this reason we deduce an activation energy for the reaction:

$$CH_3+D_2 \xrightarrow{440°K} CH_xD_y+D;$$
$$E=11.1 \text{ kcal. } (s=0.1).$$

At room temperatures such a reaction does not occur measurably, so that we must consider other methods of methane formation from the methyl radicals produced by atomic deuterium in the C−C bond split of ethane which freely occurs at room temperature. There are two possible alternative initial steps in the interaction with ethane:

$$\text{(a)}\quad D+C_2H_6=C_2H_5+HD,$$
$$\text{(b)}\quad D+C_2H_6=CH_3+CH_3D.$$

The first corresponds to the primary step in the Bonhoeffer-Harteck suggestion of a dehydrogenation-hydrogenation mechanism of "catalytic" recombination of atomic hydrogen. It would be followed by further dehydrogenation to ethylene on rehydrogenation to deuteroethanes. The negligible amounts of unsaturated products (~ 1 percent) and the absence of exchanged ethanes in the low temperature runs indicate that this reaction cannot be very important. The extensive methane formation at room temperatures indicates that reaction (b) has a small activation energy of 7.2 kcal., as previously stated.

The extensive deuterium substitution of the resulting methanes suggests that one or both products of the split must undergo further interaction with deuterium atoms (at ordinary temperatures, as seen above, reaction of methyl with hydrogen molecules is of low efficiency). The mechanism for the deuterization of the methyl radicals is easily understood. It may follow a sequence of processes such as:

$$CH_3+D\rightarrow CH_3D' \rightarrow CH_2D+H$$
$$CH_2D+D\rightarrow CH_2D_2'\rightarrow CHD_2+H$$
$$CHD_2+D\rightarrow CHD_3' \rightarrow CD_3+H.$$

This represents the formation and dissociation, before stabilization by third body collision, of quasi-methane molecules. The experimental condition of high D atom concentration relative to H would insure fairly complete conversion of CH_3 to CD_3. This would suffice to account for the observed deuterium exchanges. An alternative mechanism to this would involve dehydrogenation-rehydrogenation, thus:

$$CH_3+D=CH_2+HD,$$
$$CH_2+D=CH_2D,$$
$$CH_2+D_2=CH_2D_2.$$

There is no evidence for or against this mechanism.

We cite as additional reason for reaction (b) as opposed to a sequence of reactions:

$$C_2H_6+D=C_2H_5+HD \qquad (1)$$

and

$$C_2H_5+D=CH_3+CH_2D \qquad (2)$$

for the C−C bond split, the earlier experiments with Hill[18] in which the addition of hydrogen atoms to ethylene was studied in the temperature range 16–100°C. The evidence there obtained is decisive that the addition, through C_2H_5, to ethane was quantitative and complete before any measurable amounts of methane were formed. These data together with those of the present work indicate definitely that at ordinary temperatures the collision C_2H_6+H is a much more important method of securing the C−C bond split than the collision C_2H_5+H.

If the C−C bond in C_2H_5 is strengthened by dehydrogenation of C_2H_6 as certainly is the case when still further dehydrogenation to C_2H_4 occurs then one sees at once the reason for the results of Taylor and Hill and those found in the present investigation both of which point to the fact that C_2H_6 under the influence of H atoms splits directly to CH_3 and CH_4 at least at low temperatures.

Above 100°C the deuterization of ethane becomes marked. We ascribe this to the more frequent occurrence of the dehydrogenation reaction $C_2H_6+D=C_2H_5+HD$ followed by the recombination of C_2H_5 and D to yield deutero-ethanes, as in the experiments of Taylor and Hill. A repetition of such processes as $C_2H_5+D \rightarrow C_2H_5D' \rightarrow C_2H_4D+H_1$ increases the substitution. An alternative source of deutero-ethanes is present in the recombination process of two methyl radicals, the extent of deuterization being dependent on the deuterium content of the radicals. This recombination process, depending on the square of the methyl concentration, becomes increasingly important with the increase in stationary state concentration of methyl radicals with increase in temperature. Both these methods of producing deuteroethanes are secured at the expense of deuteromethane production which, as Table I shows, decreases in extent beyond 100°, having risen in amount up to that temperature.

At temperatures beyond 165°C the reactions $CH_3+D_2=CH_3D+D$ and $C_2H_5+D_2=C_2H_5D+D$ become important alternative methods of producing substitution (cf. *W*13 and *W*20).

The ready deuterization of methyl radicals as compared with methane is also observed in the case of the ethyl and propyl radicals from propane and butane. We may adopt a similar explanation, namely the formation and dissociation, before stabilization by third body collision, of "hot" quasi-propane and -butane molecules. As the yield of methane in every case exceeds the amount equivalent to ethane or propane which should simultaneously be formed we must conclude that a certain amount of further decomposition of these quasi-molecules to split products must occur.

In every case the data reveal that the split products from a hydrocarbon are very highly exchanged. In many cases the extent of exchange borders on the limit of that possible if the process be exemplified by the reaction $C_2H_6+D=CH_3+CH_3D$ and the deuterization of the methyl be complete. The exchange is in several cases so high as to suggest that the formation of CH_3D (and the corresponding ethane and propane with the higher hydrocarbons) does not end the substitution in that fragment of the molecule. Since normal methane molecules do not interact below 300°C this would involve the assumption that the energy available to the molecule CH_3D as a result of its formation (the reaction $C_2H_6+D=CH_3+CH_3D$ is probably 10 kcal. exothermal) is available for further reaction with atomic deuterium. A small amount of such reaction would suffice to account for observed substitutions.

Bond energies

The activation energies which we have deduced for two of the reaction processes in the methane-deuterium system permit an estimate of the magnitude of the CH_3-H bond in methane. We express these activation energies E_1 and E_2 and the consequent heat of reaction (E_2-E_1) by the equation

$$CH_4+D \underset{E_2=11.1 \text{ kcal.}}{\overset{E_1=15.6 \text{ kcal.}}{\rightleftharpoons}} CH_3+HD-4.5 \text{ kcal.}$$

For each activation energy we have assumed a steric factor $s=0.1$. Combining this with the equation:

$$HD \rightarrow H+D-103.5 \text{ kcal.}$$

we deduce for the process

$$CH_4 \rightarrow CH_3+H-108 \text{ kcal.}$$

[18] Taylor and Hill, J. Am. Chem. Soc. **51**, 2922 (1929).

This is near to the upper limit previously deduced by Polanyi and Hartel[19] (98–110 kcal.) from the reaction in CH_4+H_2 systems induced by chlorine and sodium atoms. The value of 108 kcal. is larger than can be derived from an assignment of equal energies to the four C−H bonds in methane. Our calculations show that the value is not very sensitive to the assumptions made as to steric factor, but we hope later, by greater refinements of technique and the study of other reaction systems, to give to the value a definite precision. In the meantime we believe that it cannot be in error by more than 3000 calories.

Such a value for the energy of this CH_3-H bond when combined with the most recent data on the heats of formation of methane and ethane from solid carbon (diamond) and hydrogen, leads to a startling result for the C−C bond energy in ethane. According to Bischowsky and Rossini[20] the heats of formation are

$$2C(s)+3H_2=C_2H_6, \quad \Delta H_{291}=-20.96 \text{ kcal.},$$
$$2C(s)+4H_2=2CH_4, \quad 2\Delta H_{291}=-36.48 \text{ kcal.}$$

Whence

$$2CH_4=C_2H_6+H_2, \quad \Delta H_{291}=15.5 \text{ kcal.}$$

Since

$$2CH_3+2H=2CH_4, \quad \Delta H=-216.0 \text{ kcal.},$$

and

$$H_2=2H, \quad \Delta H=102.9 \text{ kcal.},$$

we derive

$$2CH_3=C_2H_6, \quad \Delta H=-97.6 \text{ kcal.}$$

This is a surprisingly high result. Earlier values approximate to 80±6 kcal. and values as low as 65 kcal. have been discussed. All these estimates hinge in some way or other on the heat of vaporization of carbon, a factor which has consistently loaded the result with much uncertainty.[21] It is of interest to note that to bring the value for the C−C bond in ethane down to the value 80 kcal. the value for the CH_3-H bond must be lowered to 99.2 kcal. Such a figure would change the order of difference between E_1 and E_2. E_2 would be greater by 4.3 kcal. in which case it would be impossible to account for the relative ease of the reaction CH_3+HD as contrasted with the reaction CH_4+D. To bring the energy of the C−C bond down to the value of 72 kcal. recently deduced by Kistiakowsky[22] it would be necessary for the activation energy of the reaction $D+CH_4=CH_3+HD$ to be as low as 3 kcal. with a value for the activation energy of $CH_3+D_2=CH_3D$ of 11 kcal. This would be in total disagreement with our observation of the difficulty of interaction between methane and atomic deuterium. We are making further studies of these processes by other methods. The data thus obtained may permit the elimination of the steric factor from the calculation, a factor which must now be used with a considerable degree of arbitrariness.

From an investigation of the concentrations of CH_3 radicals and H atoms present in the photodecomposition of acetaldehyde between 400 and 700°K Patat[23] arrived at the activation energy for the reaction $CH_3+H_2=CH_4+H$. He found it to be 9 kcal. when the steric factor s was taken to be 10^{-4}. This was done to obtain agreement with von Hartel and Polanyi's directly observed value of 8 kcal. If, however, s be taken as unity then Patat's value becomes 20 kcal. Paneth, Hofeditz and Wunsch's[24] data on the direct reaction of CH_3 with H_2 gives an E_{act} of 15 kcal. when $s=1$ Using Geib and Harteck's estimated value of $E_{act}=17$ kcal. when $s=1$ for the reaction $CH_4+H\rightarrow CH_3+H_2$ but changing s to 10^{-4} Patat finds $E_{act}=8.7$ kcal. so that:

$$CH_4\rightarrow CH_3+H, \quad \Delta H=102.5 \text{ kcal.}$$

results. He points out that this result is in essential agreement with Polanyi's previous estimate of 110 kcal. for the C−H bond in methane, deduced from the fact that Cl atoms react rapidly with methane. The present authors intend to investigate the correctness of such a value as 10^{-4} for the steric factor s by a direct estimation of the temperature coefficient of the reaction $CH_4+D\rightarrow CH_3+HD$. We shall report such studies at a later date.

[19] von Hartel and Polyanyi, Zeits. f. physik. Chemie **11**, 97 (1931).
[20] Bischowsky and Rossini, *The Thermochemistry of Chemical Substances* (1936).
[21] See for example, Goldfinger and Jeunehomme, Trans. Faraday Soc. **32**, 1591 (1936).
[22] G. B. Kistiakowsky, J. Phys. Chem. **41** (1937). Symposium on Molecular Structure, Princeton, Dec. 1936.
[23] F. Patat, Zeits. f. physik. Chemie **32B**, 290 (1936).
[24] Paneth, Hofeditz and Wunsch, J. Chem. Soc. 372 (1935).

The Mercury Sensitized Reactions of Methane, Deuteromethanes and the Hydrogen Isotopes

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The interaction of methane and deuterium and of methane and methane-d_4 under the influence of excited mercury have been studied. The influence of temperature, reactant concentration, light intensity and mercury concentration on the yield of deuteromethanes has been measured. Below 200° the results indicate that the production of deuteromethanes is governed by the photosensitized formation of free methyl radicals. At higher temperatures chain reactions become important and high quantum efficiencies of interaction are observed. A simultaneous process of condensation of methane to yield higher saturated hydrocarbons has been shown to occur and its kinetics and quantum efficiency studied. The condensation occurs in presence of hydrogen and its isotope. A sequence of reactions has been postulated and approximate energies of activation suggested which permit a description of the observed phenomena over the whole range of temperatures, light intensity and concentrations studied.

A PRELIMINARY investigation of the mercury photosensitized reaction between deuterium and methane[3] showed that interaction with formation of deuteromethanes occurred in the range of temperatures from 40° upwards, the temperature coefficient of the reaction indicating an activation energy of the order of 5 kcal. Since the quenching efficiency of deuterium for the resonance radiation of mercury is equal to that of hydrogen[4] and is therefore large at room temperatures with respect to that of methane,[5] the preliminary results indicated that the interaction of deuterium atoms and methane should be an efficient process with a low activation energy of the order of magnitude cited. Geib and Steacie[6] and more recently Steacie and Phillips[7] have brought forward evidence which indicates that the activation energy of the reaction is about 11 kcal. In the earlier work of these authors, deuterium atoms from a Wood's discharge tube were used. In the later work, both atoms from the discharge tube and the mercury sensitized reaction were studied. Our own investigations with the latter reaction, which have continued uninterruptedly since our first communication, have revealed that the processes occurring are very complex and that an accurate determination of the activation energy of the reaction in question cannot thus be obtained since other processes are producing deuteromethanes and reactions leading to condensation products of the hydrocarbon occur. In the following pages we record in detail the results of these more comprehensive studies since they yield much information concerning the fundamental reactions of atomic hydrogen isotopes and hydrocarbon radicals.

[1] Visiting Research Fellow of the Central Laboratory, The South Manchuria Railway Co., Dairen, Japan.
[2] National Research Fellow in Chemistry, 1933–1935.
[3] Taylor, Morikawa and Benedict, J. Am. Chem. Soc. **57**, 383 (1935).
[4] Evans, J. Chem. Phys. **2**, 445 (1934).
[5] Bates, J. Am. Chem. Soc. **52**, 3825 (1930); **54**, 569 (1932).
[6] Geib and Steacie, Zeits. f. physik. Chemie **B29**, 215 (1935).
[7] Steacie and Phillips, J. Chem. Phys. **4**, 461 (1936).

EXPERIMENTAL DETAILS

Materials

Hydrogen was obtained by the electrolysis of potassium hydroxide solutions, and purified by passage over platinized asbestos at 250° and through a liquid-air trap. Deuterium was similarly prepared from a KOD$-D_2O$ solution, oxygen impurities being removed over a hot platinum wire, to avoid dilution with hydrogen by exchange reactions.

Methane was prepared by reduction of carbon monoxide with excess hydrogen on a nickel catalyst at 255°, the excess hydrogen being removed over copper-copper oxide at 300°; the carbon dioxide formed in a side reaction was removed by soda lime and the water vapor in a solid carbon dioxide-acetone mixture. Repeated fractionation of the residue at liquid-air temperatures yielded the final pure product.

Methane-d_4 was prepared in essentially the same manner. The catalyst employed was re-

duced in deuterium from the purest D_2O available. The final product was 96–98 percent C–D.

Apparatus and experimental method

A static method was employed shown in diagrammatic outline in Fig. 1. The light source *S* was a Hanovia Sc. 2537 lamp with the discharge tubing coiled into a flat spiral which could be placed parallel to the plane face of the quartz reaction tube *V*. The light from the source was normally filtered through a 25 volume percent solution of acetic acid passing continuously through the quartz cell *F*, the solution being renewed about once every half-hour. This served to eliminate the short wave-length radiation below 2537A. In a few experiments a Cl_2-Br_2 gas filter was used. The radiation was collected by the quartz lens *L* and concentrated in an approximately parallel beam on the reaction vessel *V* placed inside and to the rear of an electric furnace, the front end of which was closed with a plane parallel quartz plate, *P*. The quartz reaction vessel was cylindrical, 12.8 cm long and 4.6 cm diameter, the front plane polished face of which was 12.5 cm from the plate *P* in a furnace 30 cm long and 6.3 cm internal diameter whose temperature could be controlled to $\pm 3°$. The supply of mercury vapor to the reaction cell came from a side tube *M* in which the mercury could be maintained either at 0° with ice-water or at 56° by boiling acetone in the surrounding vessel *B*, the acetone being condensed in *C* and kept dry by the calcium-chloride tube in the position shown.

The gases could be introduced by the capillary leak *T* into the reaction vessel either saturated with mercury vapor at a controlled temperature or freed from traces of water vapor by immersing the trap shown in solid carbon dioxide-toluene mixture.

The main portion of the apparatus shown in the diagram with a reaction volume of 230 cc and total volume of 270 cc was connected through a stopcock to the manometer, to a gas burette which also served as a Töpler pump, to an analytical train (which consisted of a copper-copper oxide tube and a fractionation trap)[7a] to

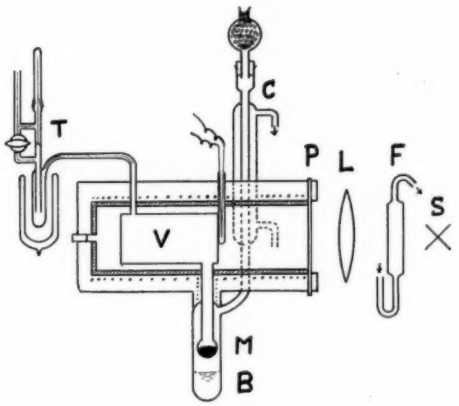

FIG. 1.

gas storage bulbs, to a McLeod gauge and to an evacuation train consisting of a mercury diffusion pump and an oil pump.

The cell could be cleaned between runs by applying an electric discharge to hydrogen in the cell at a pressure of several mm, the system being then thoroughly evacuated. The excellent reproducibility of experimental results testifies to the efficiency of this treatment after runs extending over a period of more than one year.

The light source was brought to constancy of operation by burning for at least one half-hour prior to use in an experiment. Mixtures of gases of known composition were then illuminated for a definite interval of time, the residual gases recovered by evacuation with a Töpler pump and introduced either into an analytical cell for analysis by infrared absorption or to the analytical train already described.

Analytical details

The progress of the exchange reaction between deuterium and methane and between methane and methane-d_4 was followed by measurement of the absorption at specific wave-lengths in the infrared region. This technique has already received detailed discussion.[8] The analysis was made in presence both of hydrogen and higher hydrocarbons produced during reaction, but measurements of absorption at the various wave-lengths due to one or other of the several substituted methanes served not only to give the percentage of C–D bonds in the mixture

[7a] K. Morikawa and N. R. Trenner, J. Am. Chem. Soc. **59** (1937).

[8] Benedict, Morikawa, Barnes and Taylor, J. Chem. Phys. **5**, 1 (1937).

but to identify and define the distribution of the deuteromethanes produced. In some cases the methanes were free from the higher hydrocarbons formed by fractional extraction at liquid-air temperatures and then analyzed. The results obtained by both methods were quite concordant.

The analytical data for the exchange reaction between methane and deuterium are expressed as percent C−D in the product defined by the expression, $100(C-D)/(C-H+C-D)$. The quantum efficiency γ_e, equivalent in our experiments to quantum yield, is obtained from the expression $\gamma_e = 4 \times cc_{CH_4} \times$ percent C−D$/100tI_{abs}$ since CH_4 contains four C−H bonds, and t is the time in hours, I_{abs} the intensity of resonance radiation $\lambda = 2537$A absorbed expressed in cc per hour.

The reaction between methane and methane-d_4 is expressed as percentage attainment of equilibrium θ. In this case the quantum efficiency is given by $\gamma_e' = 0.5\theta \times cc_{(CH_4+CD_4)} \times 4/100tI_{abs}$. This assumes an equilibrium constant $K=1$, equilibrium corresponding to 50 percent C−D in a CH_4+2D_2 mixture.

The condensation processes found to occur in these hydrocarbon systems were followed analytically by measuring the pressures at two constant volumes. The data in the succeeding tables refer to the pressures at a volume of 88 cc. The total gas recovered from a reaction was passed slowly through a liquid-air trap in which the higher hydrocarbons formed were solidified. The methane and hydrogen were extracted by a Töpler pump, the solid residue vaporized, recondensed and the extraction process repeated. The hydrogen-methane extraction was analyzed by passage over copper-copper oxide at 250–300°, the decrease in volume noted and the residual methane recovered through a solid carbon dioxide trap. We thus can measure the total pressure change, the amount of methane consumed ($-\Delta CH_4$), the higher hydrocarbons produced ($+\Delta H-HC$) and the hydrogen produced ($+\Delta H_2$). The average formula of the higher hydrocarbons (C_nH_m) can be learned approximately by compressing the gases, after vaporization, to 10 cc volume and measuring the vapor pressure at −80° and room temperature. The ratio of these two pressures ($P_{-80°}/P_{25°}$) is a relative index of the degree of condensation. Corrections were made for the pressure increase due to temperature rise alone. In some cases the higher hydrocarbons were oxidized on copper-copper oxide at 540° and the carbon dioxide and water formed were measured. From such data the average formula C_nH_m could be independently calculated. The calculated value of n was normally greater than the observed value owing to solution of higher hydrocarbons in the stopcock grease.

In the condensation processes the quantum efficiency, γ_c, is in every case given by the expression $\gamma_c = (-\Delta CH_4)/tI_{abs}$.

Intensity of light source

A direct measurement of the intensity of light absorbed in the reaction system was made by means of a thermopile-galvanometer system placed immediately behind the reaction vessel receiving light from the source through the acetic acid filter and lens system in its normal position. The thermopile was calibrated with the aid of a standard lamp[9] of the National Bureau of Standards. In this manner it was found that the total light energy normally falling on the system amounted to $3.1 \pm 0.3 \times 10^3$ ergs per cm^2. This was measured with an evacuated cell, with neither mercury vapor nor other gas measurably present. Of the light energy from the arc passed by the acetic acid filter, it was found that 63.6 ± 0.5 percent was the resonance radiation $\lambda = 2537$A. This was equivalent to 3×10^{-11} Einsteins per cc per sec. in the reaction system (1 Einstein $= N_A h\nu$), as calculated from the amount of maximum absorption when there was high mercury and high hydrogen or methane concentrations in the reaction vessel.

TABLE I. *Relation between arc current and light intensity. Hg at −190°; cell evacuated; acetic acid filter 25 vol. percent.*

Current (amp.)	Relative Current	Total Energy ergs/cm^2 $\times 10^{-3}$	Relative Intensity of 2537A	Energy of 2537A Percent
4.51	1.00	3.40	1.00	63.2
3.99	0.886	3.22	0.947	—
3.44	0.763	2.96	0.869	—
2.82	0.626	2.61	0.766	—
2.05	0.455	2.03	0.597	64.1
4.48	0.993	3.46	1.035	—

[9] A. L. Marshall, J. Chem. Phys. **30**, 1085 (1926).

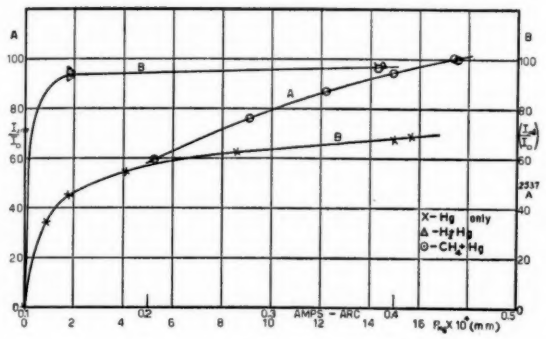

FIG. 2.

The relation between arc current and light intensity is shown in Table I and Fig. 2. The data show that while the total radiant energy emitted falls more slowly than the arc current the fraction of the energy in the form of resonance radiation remains substantially constant.

The chlorine-bromine filter was less efficient. Only 31 percent of the resonance radiation is transmitted by this filter,[9] and spectrographic measurements showed that the acetic acid filter was much superior. Data on the relative rates of the mercury sensitized reaction between hydrogen and oxygen ($2H_2+O_2$) indicate that the latter filter transmits 83 percent of the resonance radiation, if we assume that the rate of reaction varies directly as the intensity, and that Marshall's figure of 31 percent transmission for this Cl_2-Br_2 cell is correct. With the two filters, Cl_2-Br_2 and acetic acid, the rates of the sensitized reaction $2H_2+O_2$ were 2.8×10^{-11} and 7.6×10^{-11} mole per cc per sec., respectively, at a temperature of 20°. A consumption of approximately 2 mole of ($2H_2+O_2$) per Einstein absorbed would bring these data into agreement with the thermopile measurements.

Absorption of resonance radiation

A dynamic method was employed to determine accurately the variation of absorbed resonance radiation with mercury pressure in presence and absence of foreign gas. A circulating pump of the Sprengel type was attached to the reaction vessel temporarily to circulate either mercury vapor at controlled vapor pressures or foreign gases at controlled pressures saturated with mercury vapor at controlled temperatures. Circulation was continued until constant absorptions were obtained. The data obtained are exhibited in Table II and graphically in Fig. 2.

It will be noted that the fraction of resonance radiation absorbed rises at first very steeply with the mercury pressure and then more slowly to 0.69 at 15.7×10^{-4} mm Hg pressure. The addition of high pressures of either hydrogen or methane considerably *increases* the fraction absorbed, e.g., from 0.45 to 0.94 with $[Hg]=1.8\times10^{-4}$ mm and $[H_2]=0$ and 142 mm. Since methane is apparently as efficient as hydrogen, the effect cannot be due to quenching and must be attributed to pressure broadening effects.[10] Spectrophotographic measurements of the absorbed radiation gave results entirely concordant with these data.

A static method of measurement of absorption of resonance radiation gives rise to equivocal results. If gas be introduced into the reaction vessel through a trap containing mercury held at the same temperature as the mercury vapor source, the initial concentration of mercury is markedly higher than the saturated vapor pressure at the temperature in question. This is because mercury vapor is introduced by the carrier gas into a space already saturated with mercury vapor. Desaturation occurs only slowly due to the slowness of the diffusion process, and may consume many hours. Advantage may be taken of this to obtain maximum absorption of resonance radiation at room temperatures in the presence of high hydrogen or methane concentrations.*

EXPERIMENTAL RESULTS

I. The exchange reaction

(*a*) *The effect of temperature and light intensity.*—The data for the effect of temperature, from 98 to 488°, and of light intensity using the Cl_2-Br_2 and acetic acid filters are shown in Table III. The data reveal an increase in quantum efficiency of exchange, γ_e, from 0.6 at ~100° to 70 at ~490°. The temperature coefficient is not constant but increases from a value $E\sim2$ kcal. in the lower temperature range to

[10] For a contrary point of view not based on absorption measurements see Melville, Proc. Roy. Soc., **A152**, 332 (1935).

* We wish to express our thanks to Dr. N. R. Trenner for assistance in making these thermopile measurements.

14 kcal. in the high temperature range. Both these lines of evidence suggest a chain reaction of exchange increasing in length with increase of temperature.

In the low temperature range a decrease of intensity, I_0, decreases the rate (γ) but at high temperatures the reverse is true. This points definitely to a change of mechanism as the temperature is raised.

(*b*) *The effect of mercury concentration.*—The data of Table IV with the mercury at its saturation pressure at 0°, 1.8×10^{-4} mm are to be compared with the data of Table III, since in both the acetic acid filter was used. It will be noted that the effect of the lowered mercury concentration is quite similar to the effect of the decreased light intensity when the Cl_2-Br_2 filter was used.

(*c*) *Comparison of the reactions* CH_4+D_2 *and* CH_4+CD_4.—The data of Table V show that, in the absence of hydrogen, methane and methane-d_4 undergo exchange reaction. The rate is, however, much slower than in the exchange of methane and deuterium. The effect of temperature is very similar in the two cases and since the activation energy in the case of the two methanes increases from 8 to 15 kcal. in the range from 296 to 488°, a chain mechanism is indicated in this case also. The small effect of low concentrations of deuterium on the methane-methane-d_4 exchange is also to be noted.

(*d*) *Comparison of the reactions* CH_4+D_2 *and* CD_4+H_2.—The rates of these two reactions under comparable conditions are almost identical as shown in Table VI. Indeed, the reaction CD_4+H_2 appears to be somewhat the faster of the two.

(*e*) *Kinetics of the reaction* CH_4+D_2.—An examination of the effect of various concentration ratios of the two gases at the two temperatures 196 and 392°, as shown in Table VII indicate clearly that the kinetics are different at the two temperatures. The dependence on total pressure, methane and deuterium concentrations shown below the table, is calculated from a very restricted series of measurements and no precision is claimed for the exponents thus secured. They do indicate, however, very varied effects of the three variables in the two temperature regions where the quantum efficiency shows a 12-fold ratio.

(*f*) *Composition of exchanged methanes produced.*—In the low temperature runs at 98°, the composition of the products deviates considerably from the equilibrium distribution usually attained in the high temperature runs. This is revealed in Table VIII and Fig. 3.

TABLE II. *Absorption of resonance line under various conditions. Cell temp. 24°; arc current 4.5 amp.; fraction of energy as* $=2537A=0.632$.

Temp. of Hg Saturator °C	[Hg] mm $\times10^4$	Foreign Gas mm at 25°	Total Energy Falling on System ergs/cm² $\times10^{-3}$	Resonance Line Absorbed ergs/cm² $\times10^{-3}$	Fraction of Resonance Radiation Absorbed
−190	0	—	3.07	—	—
+23.1	15.7	—	1.74	1.34	0.690
+16.2	8.6	—	1.86	1.22	0.628
+7.9	4.1	—	2.02	1.06	0.547
0.0	1.8	—	2.20	0.88	0.451
−6.5	0.9	—	2.43	0.65	0.342
+22.5	15.0	—	1.76	1.32	0.679
0.0	1.8	$H_2=142$	1.21		
	1.8	$H_2=142$[1]	1.25	1.83	0.943
	1.8	$H_2=142$[2]	1.25		
−190	0	—	3.08	—	—
−190	0	—	3.17	—	—
0.0	1.8	$H_2=288$	1.31	1.84	0.926
22.1	14.5	$H_2=290$	1.21	1.94	0.975
22.0	14.3	$H_2=142$	1.22	1.93	0.969
22.0	14.3	$CH_4=141$	1.23	1.92	0.963
−190	0	—	3.12	—	—

[1] After 18 min. circulation.
[2] After 33 min. circulation.

II. The condensation reactions

(*a*) *The effect of temperature.*—Methane condenses to yield saturated higher hydrocarbons and hydrogen without pressure change under the influence of resonance radiation as revealed by the data of Table IX. At the highest temperature, ~490°, there was a small but definite pressure increase, with production of unsaturated hydrocarbons identified by analysis. The table shows that the extent of condensation, n, decreases with increase of temperature but the rate increases. A composite sample of many runs (Nos. 65–96) showed 3.8 percent unsaturates. The saturated hydrocarbons in the same composite sample were analyzed by fractionation to yield $C_2H_6\leq10$ percent; $C_3H_8\sim50$ percent; $C_4H_{10}\sim39$ percent. The data of Table IX as plotted in Fig. 4 indicate that while the initial rate of condensation progressively increases with increase of temperature the stationary state of

TABLE III. *Effect of temperature and light intensity.* r_{H_2} *at* $55° = 1.8 \times 10^{-2}$ *mm.*

No. of Expt.	CH_4 cc/25°	D_2 cc/25°	Reaction Temp. °C	Reaction Time Hrs.	C–D %	C–D cc	C–D cc/hr.	C–D γ
Cl–Br Filter, $I_t = 31\%$, $I = 0.23$ cc/hr.								
10	42.3	42.5	196	30	2.5	4.23	0.14_1	0.61
11	42.0	42.2	196	60	4.0	6.72	0.11_2	0.49
18	43.2	43.1	247	30	7.0	12.1	0.40_2	1.7_5
8	41.9	42.0	296	15.3	8.8	14.7_5	0.96_4	4.2
9	41.9	42.2	296	30	13.5	22.8	0.76	3.3
19	44.0	44.0	344	8.7	13.0	22.9	2.63	11.4
Acetic Acid Filter, $I_t = 83.1\%$, $I = 0.61$ cc/hr.								
91[2]	41.4	41.2	98	113	17.5	29.0	0.25_7	0.42
47[1]	43.3	43.2	98	31.5	6.5	11.3	0.35_9	0.59
14	43.7	43.6	196	12	4.2	7.3_4	0.61_2	1.0
15	43.7	43.6	196	6.5	2.5	4.3_5	0.66_9	1.1
48[1]	43.1	43.3	196	12	4.2	7.2_4	0.60_3	1.0
16	43.5	43.5	247	7.0	4.5	7.8_3	1.1_2	1.8_4
12	43.2	43.2	296	6.5	8.5	15.0	2.3_1	3.8
13	43.7	43.7	296	3.0	5.0	8.7_4	2.9_1	4.8
17	43.5	43.5	344	3.0	8.0	13.9	4.6_3	7.6
21	45.0	44.8	392	2.0	11.0	19.8	9.9	16.2
26	45.9	45.9	392	2.1	13.5	24.8	11.8	19.4
25	44.9	44.9	488	0.5	12.0	21.6	43.2	71

[1] Special caution was taken to dry the gas and no effect of water observed.
[2] After separation of higher hydrocarbon, C–D bonds measured.

hydrocarbon production changes with the temperature. Over a period of twenty-four hours illumination the amounts of methane converted to higher hydrocarbons increase up to a temperature of 296°, and decrease with further temperature increase. Table IX also shows that the rate of condensation increases with decrease in the mercury vapor concentration.

Fig. 4 shows that the variation of the rate of condensation with temperature is the opposite of that in the exchange reaction. Increase of temperature produces a marked effect in the low temperature range and a much smaller effect at higher temperatures. In only two cases does the quantum efficiency exceed 2, in both cases at the highest temperature, 488°.

(*b*) *Kinetics of condensation.*—The data of Table X show that the rate of methane condensation increases with increase in methane concentration, $v \propto [CH_4]^x$ but x decreases progressively with increase of temperature from 0.71 at 196° to 0.28 at 488° (Table XI).

(*c*) *Effect of H_2 and D_2 on methane condensation.*—The rate of condensation in presence of deuterium is greater than that in presence of hydrogen as Table XII shows. The temperature coefficients are remarkably similar as can be seen from Fig. 5. They are less than the temperature coefficient in absence of added gas especially in the high temperature range. A remarkable increase in the rate of condensation with added deuterium is found in the low temperature range by decreasing the mercury concentration to the saturated vapor pressure at 0°.

III. General summary of experimental results

For purposes of ready reference in the discussion which succeeds we have collected in Table XIII the mean values for quantum efficiency, γ_e, for the various reactions studied at the various temperatures. Fig. 6.

The apparent activation energies which we calculate from these data are summarized in Table XIV.

Discussion of Results

IV. General conditions in the reaction system

(*a*) *Light absorption.*—For a given condition of illumination, in accordance with Beer's law, the ratio I_{abs}/I_0 is constant. The concentration of excited mercury and, hence, *inter alia*, the deuterium atom concentration will be so distributed through the reaction system that they

TABLE IV. *Effect of vapor pressure of mercury. HAc filter.* P_{Hg} *at* $0° = 1.8 \times 10^{-4}$ *mm.*

No. of Expt.	CH_4 cc	D_2 cc	Reaction Temp. °C	Reaction Time hrs.	C–D %	C–D cc	C–D cc/hr.	C–D γ
97[1]	41.9	41.3	98	1.03	9.2	15.4	0.15	0.25
43	43.1	43.2	196	12.0	2.5	4.31	0.35_9	0.59
44	43.3	43.3	196	12.0	2.5	4.3_3	0.36_1	0.59
45	43.4	43.4	296	6.0	10.0	$17._4$	2.8_9	4.7
46	44.0	43.2	392	2.0	15.0	26.4	13.2	21.6

[1] After separation of higher hydrocarbons, C–D bonds measured.

TABLE V. *Comparison of reaction* CH_4+D_2 *and* CH_4+CD_4. *HAc filter* $= 0.61$ *cc/hr.;* $P_{Hg\ 55°} = 1.8 \times 10^{-2}$ *mm.*

No. of Expt.	CH_4 cc	D_2 cc	Reaction Temp. °C	Reaction Time hrs.	C–D %	C–D cc	C–D cc/hr.	C–D γ
40	43.0	42.8	296	6.0	9.0	17.2	2.87	4.7
21	45.0	45.0	392	2.0	11.0	19.8	9.9	16.2
26	45.8	45.8	392	2.1	13.5	24.7	11.8	19.4
25	44.9	44.9	488	0.5	12.0	21.6	43.1	71
	CH_4	CD_4			Way to eq. nil. %			
24	23.6	23.6	488	4.0	8.8	8.3	0.51_8	3.4
27	23.3	23.3	488	4.0	8.8	8.3	2.0_8	3.4
22	23.6	23.4	392	16.0	8.8	8.2	2.0_5	0.85
28	22.8	22.8	392	13.0	6.5	5.9_3	0.45_6	0.75
29	22.7	22.8	296	48	9.2	8.3_5	0.17_4	0.28
41	21.3 ($D_2=4.45$)	21.6	296	12.0	3.0	2.5_7	0.21_4	0.35
42	21.3 ($D_2=1.50$)	21.4	296	12.0	2.0	1.7	0.14_2	0.23

TABLE VI. *Comparison of reaction* CH_4+D_2 *and* CD_4+H_2. *HAc filter 0.61 cc/hr.;* $P_{Hg\ 55°} = 1.8 \times 10^{-2}$ *mm.*

No. of Expt.	CH_4 cc	D_2 cc	Temp. °C	Time hrs.	C–D %	C–D cc	C–D cc/hr.	C–D γ
37	43.0	43.0	198	12.0	3.2	5.1_6	0.43	0.71
35	43.0	42.7	296	6.0	7.0	12.1	2.0_1	3.3
40	43.0	42.8	296	6.0	9.0	15.5	2.5_8	4.2
39	42.8	42.7	392	2.0	13.5	23.1	11.5	18.9
	CD_4	H_2				C–H		
36	43.0	43.0	198	12.0	3.5	6.0_2	0.50_2	0.82
33	42.4	42.4	296	6.0	8.5	14.4	2.40	3.9
38	42.9	42.9	392	2.0	14.5	24.9	12.4	20.3

TABLE VII. *Kinetics of* CH_4+D_2. *HAc filter;* $P_{Hg\ 55°}$.

No. of Expt.	CH_4 cc	D_2 cc	Reaction Temp. °C	Reaction Time hrs.	C–D %	C–D cc	C–D cc/hr.	C–D γ
48	43.1	43.3	196	12.0	4.2	7.25	$.60_4$	1.0
49	21.3	21.4	196	12.0	5.8	4.9_4	$.41_2$	0.68
50	21.7	67.9	196	6.0	3.0	2.6	$.43_3$	0.71
51	43.7	21.7	196	8.7	4.5	7.8_6	$.90_4$	1.5
54	40.3	40.3	392	2.0	10.5	16.9	8.4_6	13.9
55	19.9	20.0	392	2.0	12.5	9.9_5	4.9_8	8.2
56	19.9	60.7	392	2.0	20.5	16.3	8.16	13.4
57	38.3	19.9	392	2.0	6.0	9.2	4.6	7.5

At 196° rate of exchange $\propto (\text{T.P.})^{+2.5}\ (CH_4)^{-0.5}\ (D_2)^{-1.5}$ At 392° rate of exchange $\propto (\text{T.P.})^{-3.2}\ (CH_2)^{+1.5}\ (D_2)^{+2.4}$

TABLE VIII. *Composition of exchanged methane from 98° runs.*

No. of Expt.	Temp. of Hg Saturator	C–D %	CH_3D% Found	CH_3D% Equil.	CH_2D_2% Found	CH_2D_2% Equil.	CHD_3% Found	CHD_3% Equil.
47	55	6.5	12	20	7	3	2	neg.
91	55	17.5	25	36	12	14	7	2
97	0	9.2	16	26	6	4.5	3	0.5

will be greatest near the front window, and will decrease exponentially with increasing distance from the window. As the concentration of mercury decreases, the reaction volume increases, thus having the effect of lowering the deuterium atom concentration and that of other decomposition fragments in the reaction volume, even though, as measurements showed, the total absorption of resonance radiation was always close to 100 percent.

(*b*) *The deuterium atom concentration.*—Farkas and Sachsse have studied in detail[11] the atomic hydrogen concentration in hydrogen-mercury mixtures illuminated by resonance radiation. They found that, with a source of resonance radiation 100 times that used in our investigations the rate of recombination of atoms was $k^1_{H_2}=3.4\times10^{16}$ cm^6 mole^{-2} sec.$^{-1}$, the atomic concentration being given by the expression, $[H]=(2I_{abs}/k^1_{H_2}[M])^{\frac{1}{2}}$. In their experiments diffusion to the wall was negligible above 200 mm total pressure. The rate of recombination of deuterium atoms will be $\sqrt{2}$ times slower or $k^1_{D_2}=2.4\times10^{16}$ cm^6 mole^{-2} sec.$^{-1}$. The D atom concentration, neglecting diffusion, and with our intensity, $I=3.0\times10^{-11}$ Einstein's cm^{-3} sec.$^{-1}$, and $[M]=[D_2]+[CH_4]=\sim13\times10^{-6}$ mole cm^{-3}, is calculable from the same equation as 13.7×10^{-12} mole cm^{-3}. These data refer to a mercury saturation at 24°. Correcting, with Farkas and Sachsse, to a saturation temperature of 55° we derive a value $[D]=\sim4\times10^{-12}$ mole cm^{-3}.

[11] Farkas and Sachsse, Zeits. f. physik. Chemie **B27**, 111 (1934).

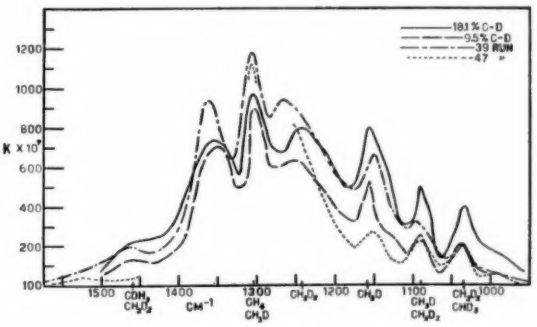

FIG. 3. Infrared spectra of deuteromethanes produced in low temperature runs.

Since the mean life of the deuterium atoms is $[D]/2I$ we derive an atom lifetime under our conditions of 6.7×10^{-2} sec. From the diffusion equation $(x^2)_{Av.}=2Dt$ we deduce that $x_{Av}=\sim0.6$ cm. This means that the atoms in approximately half the volume of our reaction cell are within diffusion range of the walls during

TABLE IX. *Effect of temperature on production of higher hydrocarbons from methane. V=88 cc. P_{Hg} at 55°. Acetic acid filter. $\gamma=(-\Delta CH_4$ in cc$)/(hrs.\times0.61)$.*

No. of Expt.	CH_4 mm	Reaction Temp. °C	Reaction Time hrs.	Recov. Gas mm	$-\Delta CH_4$ mm	$-\Delta CH_4$ cc	$+\Delta$ higher h-c mm	$+\Delta H_2$	C_n n	H_m m	$P_{-80°}/P_{25°}$	γ
58	359.0	392	18.5	359.5	43.1	4.9_9	14.2		3.0			0.43
59	355.6	392	16.0	356.5	40.7	4.71	17.1		2.1			0.48
60	359.1	392	7.0	359.9	33.4	3.8_7	16.0		2.1			0.91
61	365.8	392	4.0	366.3	29.0	3.36	12.9		2.3			1.38
62	215.9	392	4.0	216.2	20.7	2.40	9.2		2.3			0.98
66	357.2	196	16.0	357.1	22.3	2.5_8	4.9	17.5	4.5	11.1	0.46	0.265
67	359.1	196	35.5	359.2	34.3	3.9_7	6.9	28.5	5.0	11.6	0.27	0.184
68	358.2	296	17.1	357.9	43.3	5.0_2	10.8	32.6	4.0	10.0	0.45	0.48
69[2]	357.7	296	6.7		29.0	3.36	8.3	20.5	3.5	9.0	0.39	0.82
70[3]	360.8	488	4.0	362.7	26.7	3.09	11.8	16.9	2.3	6.2	0.90	1.27
73	359.2	488	12.4	362.2	35.5	4.1_1	15.8	23.3	2.3	6.0	0.92	0.54
79	359.1	196	12.0	359.4	17.5	2.03	3.9		4.5		0.49	0.28
80	359.0	296	3.0	359.1	18.3	2.12	5.8	—	3.2	—	0.69	1.16
84	358.1	488	1.1	359.2	13.7	1.59	6.0	—	2.3	—	0.98	2.6
92	360.2	98	64.5	360.2	2.7	0.31	0.5	—	5.4	—	0.73	0.008
93	357.4	296	3.2	357.9	19.2	2.2_2	8.0	—	2.4	—	0.69	1.14
				P_{Hg} at 0°								
95	356.3	196	12	356.4	20.2	2.3_4	4.5	—	4.5	—	0.47	0.32
96[1]	354.6	196	9	354.3	14.5	1.6_8	3.9	—	3.7	—	0.57	0.31

[1] I_0 was a little weaker.
[2] By expt. $C_{2.8}H_{7.5}$.
By expt. $C_{2.1}H_{5.5}$.

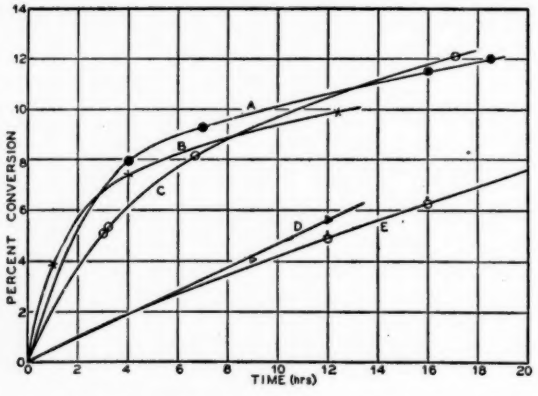

FIG. 4. Effect of temperature on the condensation of methane. Curve *A*, CH_4+H_2, 392°C, Hg at 55°C; *V*, CH_4+H_2, 488°C, Hg at 55°C; *C*, CH_4+H_2, 296°C, Hg at 55°C; *D*, CH_4+H_2, 196°C, Hg at 0°C; *E*, CH_4+H_2, 196°C, Hg at 55°C.

their mean lifetime. It is obvious, therefore, that under our experimental conditions diffusion cannot be neglected, and at the higher temperatures becomes increasingly prominent, since D varies as $T^{\frac{3}{2}}$. The difficulty of securing uniform temperature in the reaction system also suggests that convection currents will emphasize this effect.

(*c*) *Calculation of activation energy from the absolute rate of exchange in* CH_4+D_2.—Neglecting any disappearance of atomic deuterium due to such effects we calculate from the atom concentration, that, if the reaction were $CH_4+D=CH_3D+H$, the activation energy at 100° would be 14 kcal. If we assume one order lower atom concentration the activation energy would be 12.5 kcal. Table XIV shows an observed activation energy of 2–3 kcal. We conclude therefore that the exchange reaction at 100° cannot be the simple reaction, $CH_4+D=CH_3D+H$. This is confirmed by our inability to secure this reaction with atomic deuterium from a discharge tube as we shall report later. We are compelled

TABLE XI. *Kinetics of condensation of* CH_4. *Rate* $\propto[CH_4]^x$.

Temp. °C	x
196	0.71
392	0.46
488	0.28

therefore to look for the mechanism of exchange via fragments of methane, especially CH_3.

(*d*) *Quenching by methane.*—In spite of the experiments of Bates,[5] much of our work suggests that quenching of excited mercury by methane actually occurs, yielding CH_3 and H as fragments. We call attention to the possibility that this may occur directly and also by collision with metastable mercury atoms.[12] The occurrence of exchange and condensation in methanes rigorously freed from hydrogen and water vapor (*I*, *c*) is one such piece of evidence. The negligible influence of small amounts of deuterium on the exchange reaction between the methanes (*I*, *c*) at higher temperatures is further evidence that quenching by methane must be an important primary process. The relative rates of exchange in the systems CH_4+D_2 and CD_4+H_2 (*I*, *d*) constitute additional evidence. The latter reaction is somewhat faster. If the main reactions were CH_4+D and CD_4+H we would expect the latter to be the slower. If, on the other hand, the main reactions are CH_3+D_2 and CD_3+H_2 we may expect a compensation of effects. Quenching by CH_4 may be faster than by CD_4 but CH_3+D_2 should be slower than CD_3+H_2. The abnormal composition of the deuteromethanes produced at low temperatures (*I*, *f*) would not be expected if the exchange reaction proceeded via deuterium atoms and methane but is understandable if the

[12] Melville, reference 10, has considered the role of metastable atoms in the sensitized decomposition of ammonia and ammonia-d_3.

TABLE X. *Effect of concentration of methane on production of higher hydrocarbons.* P_{H_2} *at 55°. Acetic acid filter.*

No. of Expt.	CH_4 mm	Reaction Temp. °C	Reaction Time hrs.	Recov. Gas mm	$-\Delta CH_4$ mm	$-\Delta CH_4$ cc	$+\Delta$ higher h-c mm	$+\Delta H_2$ mm	C_n n	H_m m	$P_{-80°}/P_{25°}$	γ
63	356.1	392	4.0	356.4	25.0	2.90	7.9	17.4	3.2	8.3		1.19
64	202.1	392	4.0	203.0	20.0	2.32	6.1	14.4	3.3	8.4		0.95
55	707.9	392	4.0	708.5	37.0	4.28	13.8	24.4	2.7	7.2		1.76
79	359.1	196	12.0	359.4	17.5	2.03	3.9		4.5		0.49	0.28
81	708.0	196	12.0	708.4	28.5	3.30	6.5		4.3		0.54	0.45
83	703.0	488	1.0	703.9	16.6	1.92	8.1		2.1		1.00	3.15
84	358.1	488	1.0	359.2	13.7	1.59	6.0		2.3		0.98	2.6

TABLE XII. *Effect of H_2 and D_2 on production of higher hydrocarbons. P_{Hg} at 55°. Acetic acid filter.*

No. of Expt.	CH_4 mm	H_2 mm	Reaction Temp. °C	Reaction Time hrs.	$-\Delta CH_4$ mm	$-\Delta CH_4$ cc	$+\Delta$ Higher *h-c* mm	C_n	$P_{-80°}/P_{25°}$	γ
71[2]	357.2	357.7	392	12.3	17.3	2.00	7.9	2.2	0.95	0.27
72	360.9	363.7	392	21.0	16.4	1.90	7.8	2.1	0.95	0.15
74	365.0	365.4	296	17.0	24.7	2.86	6.8	3.6	0.52	0.28
75	358.7	357.9	296	5.9	16.0	1.85	5.2	3.1	0.67	0.51_5
76	359.3	360.7	196	22.5	21.5	2.49	4.4	4.9	0.34	0.18
77	358.0	356.6	196	13.5	15.8	1.83	3.7	4.3	0.43	0.22
78	355.9	352.3	196	17.0	18.0	2.08	3.9	4.6	0.39	0.20
		D_2								
85	357.0	371.6	196	12.0	26.7	3.09	5.6	4.7	0.69	0.42
86	359.8	368.8	196	5.0	15.5	1.80	4.3	3.6	0.67	0.59
87	359.4	364.8	296	5.0	23.7	2.75	6.7	3.5	0.61	0.90
88	359.4	355.8	296	3.0	17.5	2.03	5.3	3.3	0.72	1.1_1
89	358.6	360.4	296	17.0	36.7	4.25	9.9	3.7	0.51	0.41
90	358.4	380.9	98	24.1	2.6	0.30	0.9	3.1	0.87	0.02
91[1]	358.7	356.3	98	113	6.2	0.7_2	1.1	5.1	0.49	0.01
94	375.4	18.7	98	65	3.2	0.37	0.5	6.4	0.76	0.009
		$D_2 P_{Hg}$ at 0°								
97[1]	364.1	363.6	98	103	39.7	4.60	4.4	9.0?	0.40	0.073
98	357.0	357.0	196	7.0	17.7	2.05	4.4	4.0	0.54	0.48
99	354.9	358.5	196	10.0	22.5	2.61	5.5	4.1	0.48	0.43

[1] After separation of higher hydrocarbons, C−D bonds were measured.
[2] By expt. $C_{2.0}H_{5.8}$, by cal. $C_{2.2}H_{6.4}$.

TABLE XIII. *Quantum efficiencies in exchange and condensation reactions.*

Reaction	Reactants	Hg Saturation Temp. °C	Temperature °C 488	392	344	296	247	196	98
Exchange	CH_4+D_2[a]	55			11.4	4.2	1.8	0.61	
Exchange	CH_4+D_2[a]	55	71	19.4	7.6	4.3	1.8	1.1	0.59
Exchange	CH_4+D_2[a]	0		21.6		4.7		0.59	0.25
Exchange	CD_4+H_2	55		20		3.9		0.82	
Exchange	CH_4+CD_4	55	3.4	0.80		0.28			
Condensation	CH_4	55	2.7	2.1		1.4		0.29	0.008
Condensation	CH_4	0						0.32	
Condensation	CH_4+D_2	55				1.4		0.68	0.02
Condensation	CH_4+D_2	0						0.59	0.07
Condensation	CH_4+H_2	55				0.63		0.24	

[a] Cl_2-Br_2 filter used; in all other cases, acetic acid filter.

TABLE XIV. *Calculated activation energies (kcal.) in exchange and condensation reactions.*

Reaction	Reactants	Hg Saturation Temp. °C	488	392	344	296	247	196	98
Exchange	CH_4+D_2[a]	55			←14→	←11→	→10→		
Exchange	CH_4+D_2[a]	55	←14→	←11→		←7→		←2→	
Exchange	CH_4+D_2[a]	0		←12→		←10→		←3→	
Exchange	CD_4+H_2	55		←13→		←8→			
Exchange	CD_4+CH_4	55	←15→	←8→					
Condensation	CH_4	55	←3→			←8→		←13→	
Condensation	CH_4+D_2	55				←4→		←13→	
Condensation	CH_4+D_2	0						←7→	
Condensation	CH_4+H_2	55				←5→			

[a] Cl_2-Br_2 filter used; in all other cases, acetic acid filter.

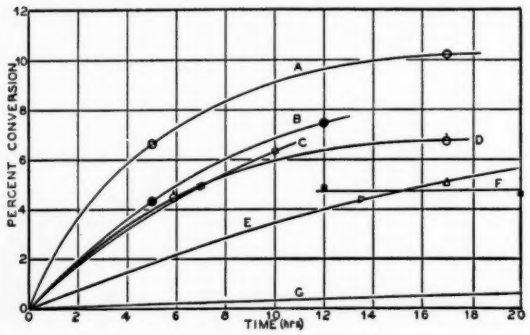

FIG. 5. Effect of H_2 and D_2 on the methane condensation. Curve *A*, CH_4+D_2, 296°C, Hg at 55°C; *B*, CH_4+D_2, 196°C, Hg at 55°C; *C*, CH_4+D_2, 196°C, Hg at 0°C; *D*, CH_4+H_2, 296°C, Hg at 55°C; *E*, CH_4+H_2, 196°C, Hg at 55°C; *F*, CH_4+H_2, 392°C, Hg at 55°C; *G*, CH_4+D_2, 98°C, Hg at 55°C.

exchange is between CH_3 and D. Evidence presented in the preceding paper[13] indicates rapid exchange between methyl radicals and atomic deuterium but none below ~300° between D atoms and CH_4. The increased rate of condensation with decrease of light intensity and mercury concentration as well as the variation in the rate of condensation with temperature (*II*, *a*) also point to a primary dissociation to CH_3 and H. The hydrogen atoms diffuse rapidly to the walls and the condensation reaction, involving combination of radicals such as CH_3+CH_3, occurs, in part at least, as a bimolecular association in the gas phase. Our evidence indicates that the recombination CH_3+H as a gas reaction is much less efficient (See *V*, (*f*)). From all these lines of evidence we conclude that quenching by methane is an important primary process representable by the equation:

$$CH_4+Hg(^3P_0 \text{ or } ^3P_1)=CH_3+H+Hg,$$
$$CD_4+Hg(^3P_0 \text{ or } ^3P_1)=CD_3+D+Hg.$$

We now consider this conclusion in reference to Bates' observations. From the data of $I(f)$ at 98°, Table VII, expt. 47, on the abnormal distribution of deuterium in the products we conclude that the CH_3 produced is not equal to the C−D exchanged. The excess CH_2D_2 over the equilibrium is $2(7-3)=8$ percent C−D; the excess CHD_3 is $3\times2=6$ percent, an excess in all of 14 percent. The total C−D exchanged is 26 percent. Therefore, it follows that a primary dissociation product CH_3 must undergo on the average one exchange, $CH_3+D=CH_2D+H$ before being stabilized.* Therefore, the quantum efficiency γ for expt. 47 should be $0.59/2=0.3$ for the primary dissociation process instead of the observed value. Combining this with the $\gamma=1.1$ at 196° where the ratios of products obey the equilibrium relationships we conclude that the activation energy of the corrected γ is 4.6 kcal. A similar calculation with expt. 97, Table VII, gives ~4.3 kcal. or a mean value of 4.4 kcal. Using this value we calculate a γ at 20° of ~0.086 which is not much greater than would be expected from Bates' quenching data at room temperatures. We suggest, therefore, a quenching efficiency for methane increasing with temperature with an activation energy of ~4.5 kcal.

With methyl radicals as well as hydrogen atom isotopes in the reaction system it is quite evident that the secondary processes are not simple and all possible combinations of methyl radicals, hydrogen atoms and molecules and methane may be involved even in the initial stages and that, in the later stages, higher hydrocarbon molecules and fragments may participate in the mechanisms.

V.

(*a*) *The possible reactions.*—We classify the possible processes in terms of (a) the primary processes, (b) the secondary processes predominating at lower temperatures, (c) the secondary processes predominating at higher temperatures and (d) later reactions of condensation and decomposition. Our selection is based upon evidence we have accumulated, and are still obtaining, in reference to the occurrence of individual reactions in particular temperature ranges. A broad program of study is in progress designed to yield definitive values for the activation energies of these atom or radical reactions with molecules. The activation energies here cited must be regarded as tentative but in agreement with our best available data.

(a) Primary processes

(1) $Hg+h\nu \longrightarrow Hg'$

(2) $Hg'+D_2 \longrightarrow Hg+2D$

(3) $Hg'+CH_4 \xrightarrow{\sim 4.5} Hg+CH_3+H$

[13] Trenner, Morikawa and Taylor, J. Chem. Phys. **5**, 203 (1937).

* For the same effect independently observed see reference 13.

(b) Secondary processes at lower temperatures (<200°)

(4) $D+D \xrightarrow{M \text{ or wall}} D_2$

(5) $CH_3+D \xrightarrow{M \text{ or wall}} CH_3D$

(6) $CH_3+D \xrightarrow{\leq 5} CH_2D+H \text{ or } CH_2+HD$

(7) $CH_3+CH_3 \xrightarrow[\text{in part}]{\text{Bimol}} C_2H_6$

(c) Secondary processes in the higher temperature range

(8) $CH_3+D_2 \xrightarrow[S=0.1]{11} CH_3D+D$

(9) $CH_4+D \xrightarrow{15} CH_3+HD$

(10) $CH_3+CD_4 \xrightarrow{11\text{–}15} CH_3D+CD_3$

(d) Later reactions of condensation and decomposition

(11) $C_2H_6+D \xrightarrow{11} C_2H_5+HD$

(12) $C_2H_5+CH_3 \xrightarrow{\text{Bimol}} C_3H_8$
or $CH_3+CH_2 \longrightarrow C_2H_5$

(13) $C_2H_6+D \xrightarrow{\sim 7.5} CH_3D+CH_3$

(14) $C_2H_6+Hg' \xrightarrow{0} C_2H_5+H+Hg$
$\searrow 2CH_3+Hg$

(15) $CH_3+CH_4 \xrightarrow{\sim 16} C_2H_6+H$ (?)

There is some evidence that reaction (15) may occur at temperatures above 400°.

(*b*) *The mechanisms at various temperatures.*—In the low temperature range, exchange will be mainly by recombination of methyl and atomic deuterium, with exchange also leading to abnormal substitution by reaction (6), which we know to have a low activation energy. The quantum efficiency will be small and determined mainly by the efficiency of (3). Around 200° the exchange by (8) sets in, and only around 300° does reaction (9) become marked.[13] A chain reaction sequence now becomes possible, and hence an increasingly rapid rise in γ.

In the condensation process, recombination of alkyl radicals must be the mechanism whereby higher hydrocarbons are produced. At the low temperatures the primary process (3) will be the sole source of these radicals, and these will be, in the main, methyl radicals only. Other radicals will arise only as the concentration of higher hydrocarbons builds up to measurable quantities. At sufficiently higher temperatures both methyl radicals and atomic hydrogen or deuterium can be regarded as sources of alkyl radicals, in the case of the atoms by reason of reaction (9). Whether the primary process is methane or hydrogen dissociation at these higher temperatures the maximum potential yield of radicals is two per quantum, unless reactions of the type (15) occur; these might increase the quantum yield slightly beyond 2.

How these mechanisms may be used to interpret the great bulk of the experimental results obtained may now be considered.

(*c*) *Temperature and the exchange reaction.*—In the low temperature range, reactions (2) to (6) are alone important. The sensitized decomposition of the methane is the rate determining factor and this, as we have shown, has an activation energy of ~4.5 kcal. We anticipate lower observed activation energies than this, since recombination of methyl radicals will decrease exchange and, owing to increased stationary state concentration of methyl, will become more important as temperature increases within the range of temperature in which the secondary

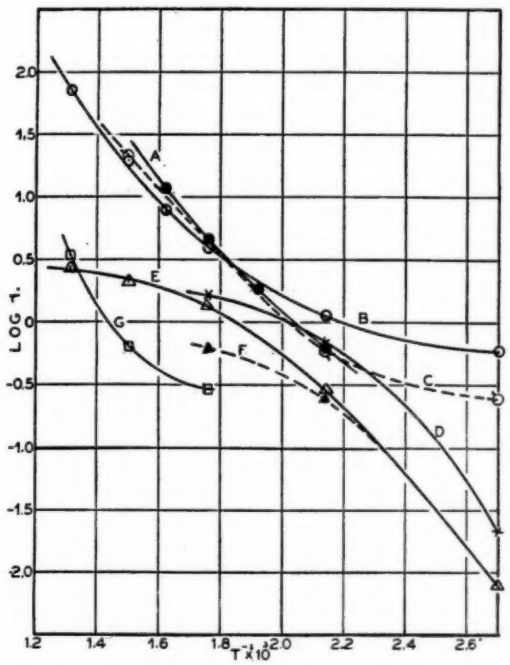

FIG. 6. Exchange: curve *A*, $CH_4+D_2-Cl_2-Br_2$; *B*, CH_4+D_2—acetic acid; *C*, CH_4+D_2, Hg at 0°C. Condensation: *D*, CH_4+D_2; *E*, CH_4; *F*, CH_4+H_2; *G*, CH_4+CD_4.

chain-producing reactions are not yet markedly occurring. We account thus for the observed values of 2–3 kcal. for the activation energy of exchange in the range 98–196°.

The continuously increasing temperature coefficient from 200° upwards points to the increasing operation of the chain reactions (8) and (9).

(*d*) *Temperature and the condensation reaction.*—The reverse behavior is to be expected in the case of condensation. Here, at low temperatures, the apparent activation energy is high and decreases steadily with increase of temperature. In the low temperature range this is due to the process of condensation involving the square of the methyl radical concentration, the production of each radical requiring ~4.5 kcal. activation energy. The decrease in temperature coefficient at high temperatures is obviously due to the limitation of quantum efficiency to 2 save for reactions of type (15).

(*e*) *The kinetics of the exchange reaction.*—The data of (*Ie*) on kinetics fit closely into the assumed mechanisms especially as to the opposite effects of the total pressure factor at low and high temperatures. At low temperatures, increased total pressure increases atom-radical recombination in the gas phase, therefore favors exchange. At lower total pressures, owing to the faster diffusion of the atoms, more hydrogen atom recombination on the walls will occur and hence more condensation and less exchange. At the higher temperatures, where the chain mechanisms (8) and (9) are predominant, the effect of increased total pressure will be to reduce exchange below what occurs at lower pressures and the same temperature since the three-body recombinations are assisted at the higher pressures at the expense of exchange-producing chain reactions (8) and (9). The negative effects of hydrogen and methane pressures at low temperatures and the positive effects at high temperatures (*Ie*) are to be interpreted similarly with the mechanisms assumed.

(*f*) *The relative velocities of CH_4 condensation and CH_4-CD_4 exchange.*—In the temperature range investigated, 296–488°, the condensation process is the more rapid, in spite of its lower temperature coefficient in this range. This can only be explained if we assume that the efficiency of recombinations such as CH_3+CH_3 is much greater than the atom-radical recombination $H(D)+CH_3$. We conclude therefore that the former approximates more to a bimolecular association reaction than the latter, which appears to require a third body or wall as stabilizer.

(*g*) *The relative velocities of condensation in CH_4+D_2 and CH_4+H_2 and CH_4 systems.*—Condensation is more rapid in the deuterium-containing than in the hydrogen-containing system. We ascribe this to a higher methyl radical concentration in the system due to a lower rate of reaction of methyl with deuterium than with hydrogen; a higher activation energy for the reaction with deuterium is intrinsically probable.

In the same way, we ascribe the higher velocity of condensation of methane alone over methane-hydrogen mixtures to the influence of greater atomic hydrogen concentration in reducing methyl concentrations in the methane-hydrogen system.

(*h*) *The effect of light intensity and mercury concentration.*—Decrease of light intensity or of mercury concentration will tend to decrease exchange and increase condensation at the lower temperatures. Both conditions lead to decrease in the stationary state concentrations of methyl and atom. Owing to the more rapid diffusion of atoms to the wall, the wall recombination of hydrogen (3) will be favored, and the exchange reactions (4) and (5) correspondingly decreased. The kinetically more efficient union of two methyl groups will therefore tend to increase, thus accounting for the increase of condensation observed with decrease of mercury concentration at 98°. As the chain-making secondary processes set in this effect of intensity and mercury concentration will disappear due to the increased role which the chain reactions play in the total observed change.

We suggest that the velocity of methane condensation which, at 98°, is smaller than that of CH_4+D_2 mixtures, although the deuterium is an active competitor for the exciting radiation, may be in part due to such causes. The presence of deuterium or hydrogen in the system is equivalent to a decrease in light intensity available for methane dissociation and we may therefore expect an enhancement of condensation to result.

(*i*) *The abnormal distribution of the deuteromethanes at 98°.*—At this temperature the main deuteromethane producing process is reaction (5). If the final stabilization is preceded by the formation of unstable quasimolecules CH_3D which dissociate before they can be stabilized, this will tend to give methanes rich in deuterium and an abnormal nonequilibrium distribution of the products. At higher temperatures, the other methane forming processes occurring progressively more rapidly will tend to yield the normal equilibrium distribution of deuteromethanes.

The observed reactions are therefore all satisfactorily interpreted by the sequence of processes postulated. They demonstrate unequivocally in their quantitative aspects the chain character of radical reactions in hydrocarbon-hydrogen (or deuterium) systems at temperatures above 200°. The experimental results are also of importance therefore in pyrolytic reactions which involve hydrocarbon radicals. Further work in progress in this general field will, it is expected, provide still more accurate quantitative data on the velocities of the individual processes.

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Raman Spectra of Amino Acids and Related Substances

III. Ionization and Methylation of the Amino Group[1]

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Raman spectra have been determined for methylated amines, and the corresponding ammonium chlorides in water; also for ethylamine and its hydrochloride, and the hydrochlorides of hydroxylamine, hydrazine and trimethylamine oxide. The spectra of the hydrochlorides arise only from the positively charged ammonium ion, since the chloride ion is not attached by any covalent bond, and, therefore, is not directly involved in any of the observed vibrations. Thus the spectrum of a methylated ammonium ion is found to be exactly similar in type to that of the analogous hydrocarbon in which a C atom is substituted for the positively charged N atom. If the $-CH_3$ and $-NH_3$ groups are treated schematically like single atoms of the same mass, all these compounds may be represented by simple models. The characteristic frequencies of such models may be correlated with lines in the observed spectra. Qualitative polarization measurements have been made on several of the substances studied and have proved of value in assigning observed frequencies to modes of molecular vibration. Bond force constants and valence angles have been evaluated for many of the substances studied, making use of certain approximate potential functions frequently employed in describing systems of this sort. In the solution of hydrazine dihydrochloride, certain Raman lines arise from the ion $^+H_3N\cdot NH_3^+$; others from $^+H_3N\cdot NH_2$. Both ions are present in appreciable concentrations, and their relative amounts are roughly what would be expected from known data on dissociation constants. The Raman spectra of the amines here studied in aqueous solution are nearly identical with those reported by other observers for the same amines as anhydrous liquids. The characteristic valence vibrations of the uncharged amino group, between 3300 and 3400 cm^{-1}, are absent in the charged $-NH_3^+$ or NH_2^+ group, being apparently replaced by much weaker lines of lower frequency. The sodium salts of glycine and alanine show strong Raman lines above 3300 cm^{-1}, which are absent in the isoelectric amino acids. This fact supplies further evidence that the amino acids exist as electrically charged dipolar ions, $^+H_3N\cdot R\cdot COO^-$.

INTRODUCTION

FROM the standpoint of the electronic theory of valence, the positively charged nitrogen atom is an almost exact analog of the carbon atom. The ammonium ion corresponds in structure to methane, the methyl ammonium ion to ethane, the tetramethyl ammonium ion to tetramethyl methane, and so forth. Thus two series of exactly analogous compounds exist.[2]

From the point of view of chemical behavior, this underlying similarity is often obscured, because the ammonium derivatives can exist only in association with suitable anions as salts. The physical properties of the latter are, of course,

[1] A preliminary discussion of part of this work has already appeared in Science **84**, 423 (1936).

[2] N. V. Sidgwick, *The Electronic Theory of Valency* (Oxford, 1927). See especially Chapters IV and XIII.

radically different from those of the analogous hydrocarbons. In the Raman spectra of substituted ammonium halides, however, the intimate relation between the two series of compounds is directly revealed; for such spectra are produced only by the vibrating cations—the isolated halide ions containing no covalent bonds and, therefore, giving rise to none of the observed vibrations. Under these circumstances, the close similarity in pattern between the ammonium ions and the corresponding hydrocarbons stands forth clearly.

The spectra of the methylated ammonium ions, from the monomethyl to the tetramethyl derivative, have now been studied, and the results are here reported. Similar studies on the analogous hydrocarbons have already been carried out.[3–5] These compounds may be approximately represented by simple models whose fundamental frequencies may be correlated with the observed Raman spectra.

In addition to these salts, three very simple ammonium derivatives have been studied. These are hydroxyl amine hydrochloride—the hydroxyl ammonium ion being structurally analogous to methyl alcohol—and the two hydrochlorides of hydrazine, which are intimately related in structure to ethane and methyl amine.[6]

The Raman spectra of methyl, ethyl, dimethyl and trimethyl amines in aqueous solution have also been reinvestigated and a number of new lines are here reported. Comparison of an amine with its hydrochloride reveals the effect on the Raman spectrum of the addition of a proton to the molecule. Chemically, such a change is one of the smallest which a molecule can experience, but, through electrostatic and other effects, it may produce far-reaching alterations in the adjoining chemical linkages. It is found that many Raman frequencies are left almost unaltered by ionization, while certain others are profoundly modified. The study of such changes should lead to a deeper understanding of the process of ionization itself. Comparison with the recent studies of Ananthakrishnan[6] and Kohlrausch[7] on anhydrous amines reveals certain effects of hydration on the Raman spectrum.

Comparative studies on the ionization of related molecules also contribute valuable information concerning structure; thus, a comparison of the ionized and unionized amines with two amino acids—glycine and alanine—and their sodium salts yields further strong evidence for the dipolar ionic structure of the amino acids.

Qualitative polarization measurements, which permit the classification of Raman lines, as definitely polarized or (approximately) depolarized, have been made for several of the compounds studied. Although the measurements are not quantitative, they have proved of great value in determining the assignment of Raman lines to particular modes of vibration in the molecule.

Experimental

The Raman spectra were photographed with a Hilger E-439 spectrograph, the technique being essentially the same as that described in the first two papers of this series.[8, 9] To isolate the mercury line at 4358A, a dilute solution of *p*-nitrotoluene in alcohol,[10, 11] was employed, which proved very satisfactory. To isolate 4047A, a very dilute sodium nitrite solution in conjunction with Corning red-purple ultraglass was employed. Separate exposures were taken for every substance investigated, using both the 4047 and the 4358 mercury lines as exciting sources.

The solutions of the recrystallized amine hydrochlorides were always acidified with excess HCl, shaken with purified charcoal (Norit) and slightly warmed, and filtered through a fine-pore filter paper. It has generally been our practice to wash out the filter paper previously with distilled water. This appears to be helpful in removing a few fine particles which may be present in the pores of the paper. The use of Norit to clarify the solutions in filtration has been previously recommended[8] and here again

[3] K. W. F. Kohlrausch and F. Köppl, Physik. Chemie **B26**, 209 (1934).
[4] D. H. Rank, J. Chem. Phys. **1**, 572 (1933).
[5] R. Ananthakrishnan, Proc. Indian Acad. Sci. (Bangalore), **3A**, 527 (1936).
[6] These compounds have also recently been studied by R. Ananthakrishnan, Proc. Indian Acad. Sci. **4A**, 204 (1936).
[7] K. W. F. Kohlrausch, Monatsh. Chem. **68**, 349 (1936).
[8] J. T. Edsall, J. Chem. Phys. **4**, 1 (1936).
[9] J. T. Edsall, J. Phys. Chem. **41**, 133 (1937).
[10] W. West and M. Farnsworth, J. Chem. Phys. **1**, 402 (1933).
[11] W. R. Angus and A. H. Leckie, Proc. Roy. Soc. **A149**, 327 (1935).

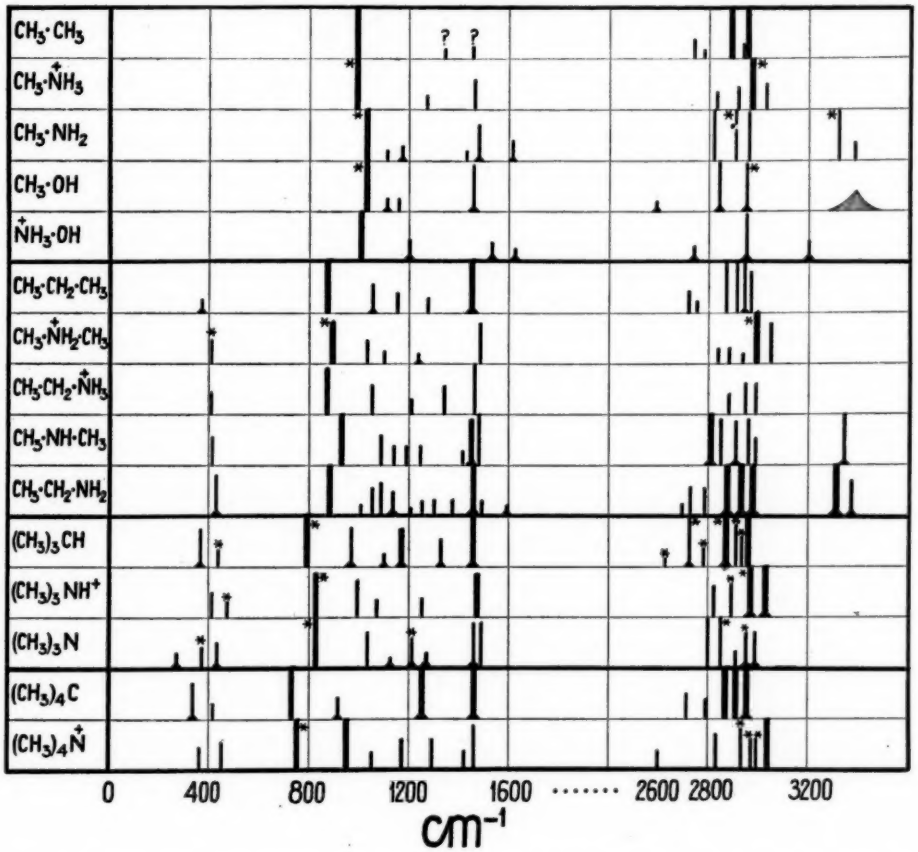

FIG. 1. Raman spectra of amines, ammonium ions and related hydrocarbons. Lines known to be strongly polarized ($\rho \ll 6/7$) are marked with an asterisk.

has given excellent results. The presence of excess hydrochloric acid (which in water is completely dissociated and gives rise to no Raman lines) greatly promotes clarification, and also represses hydrolysis of the amine hydrochlorides. With moderate care, filtered solutions are thus obtained which in optical clarity compare not unfavorably with liquids purified by distillation.

The solutions of the free amines were prepared by treating the amine hydrochlorides, dissolved in water, with concentrated sodium hydroxide, in a distilling apparatus of the type described by Kohlrausch.[12] The distillate, which came over on gentle heating, was collected directly in the Raman tube. A salt solution at $-5°$ or below was kept flowing through the condenser jacket during distillation to prevent loss of the volatile amines. As soon as distillation was complete, the Raman tubes were closed tightly with ground-glass stoppers.

The sodium salts of glycine and alanine were prepared from the recrystallized amino acids by addition of one equivalent of sodium hydroxide. It proved extremely difficult to make these solutions optically clear enough to produce thoroughly satisfactory Raman spectra. Norit cannot be used in alkaline solutions, as it always liberates traces of a fluorescent impurity which pass into the filtrate; and filtration without Norit always leaves a number of fine particles behind. The technique finally adopted was to filter the solutions through fine-pore filter paper, without Norit or any adsorbing agent, directly into the Raman tube. Filtration was slow, and, during the process, the filter and Raman tube were placed in a closed desiccator, which also contained a beaker of potassium hydroxide to absorb any carbon dioxide present in the air in

[12] K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Berlin, 1931), p. 41.

the desiccator. When filtration was complete, the Raman tube was stoppered tightly with a ground glass stopper and allowed to stand for twenty-four to forty-eight hours before the exposure was taken. During this period, most of the suspended particles remaining in the liquid settled out and adhered to the walls of the tube, and the spectra obtained were much clearer than when the exposure was made immediately after filtration.

Polarization measurements (Table V) were made using polarized incident light, which was produced by inserting a disk of Polaroid[13] between the filter tube and the Raman tube. The Polaroid could be oriented so as to transmit light with electric vector either parallel or perpendicular to the axis of the Raman tube. This method was suggested to me by Professor E. B. Wilson, Jr. In a later joint report, we propose to consider its application to more exact determination of the polarization of Raman lines.

Complete details of the observed Raman spectra with information regarding preparation and purification of materials will be found in Table IV.

Spectra and Structure of Amines and Methylated Ammonium Ions

The molecules and ions studied fall into several classes, depending on the number of heavy atoms—that is, atoms other than hydrogen—in the molecule. In Fig. 1, the first five compounds shown contain two, the next five contain three, the next three contain four, and the last two contain five such heavy atoms. The characteristic vibrations of this heavy "skeleton" are of relatively low frequency, giving rise to Raman lines in the region below 1050 cm^{-1}. In calculating the frequency of such vibrations, we may approximately represent a $-CH_3$ or $-NH_3^+$ group by a single atom of the same mass; a procedure already adopted by several investigators[3-5] in treating similar molecules. Thus the methyl ammonium ion may be considered as a diatomic molecule; the dimethyl ammonium ion as a bent triatomic molecule; the trimethyl ammonium ion as a pyramidal structure, similar to ammonia; and the tetramethyl ammonium ion as a regular tetrahedron. The same is true of the analogous hydrocarbons, whose spectra are represented in Fig. 1 beside those of the corresponding amines and ammonium ions.

Table I. *Approximate force constants for the bonds in certain ions and molecules of the ethane type.*

No.	Molecule or Ion	Bond	Frequency (cm^{-1})	$1/\mu$	f(dyne $cm^{-1} \times 10^{-5}$)
1	H_3C-CH_3	C−C	990	0.1332	4.31
2	$H_3C-{}^+NH_3$	C−N^+	995	0.1255	4.63
3	H_3C-NH_2	C−N	1034	0.1290	4.86
4	H_3N^+-OH	$^+$N−O	1006	0.1213	4.90
5	H_3C-OH	C−O	1032	0.1255	4.86
6	$H_3N^+-{}^+NH_3$	$^+$N−N^+	1036	0.1176	5.37
7	$H_3N^+-NH_2$	$^+$N−N	965	0.1212	4.54
8	H_2N-NH_2	N−N	876	0.1248	3.59

The value for ethane (No. 1) is taken from Kohlrausch (reference 12, p. 154); that for hydrazine (No. 8) is from Kahovec and Kohlrausch, *Wiener Anzeiger*. No. 16 (1936); that for the methyl ammonium ion (No. 2) is from Edsall (reference 8); other values from the present investigation. References to others who have studied these same substances are given in Table IV at the end of the paper. The assignment of the N−N valence frequency for $^+H_3N \cdot NH_2$ and $H_2N \cdot NH_2$ is slightly uncertain (see text).

[13] Obtained from the Polaroid Corporation, Boston, Mass.

The similarity of the three classes of compounds is immediately apparent from the figure. Indeed the spectra of the substituted ammonium ions bear an even closer resemblance to those of the analogous hydrocarbons than to those of the amines, as might be expected from their closer similarity in electronic configuration. In the region below 1050 cm^{-1}, where the fundamental frequencies of the molecular skeleton may be expected to lie, the similarity is particularly evident. This character of the spectra appears quite incompatible with the presence of a covalent bond between the chloride ion and any of the ammonium ions studied. Thus these observations are in harmony with the view that all these salts are completely dissociated in aqueous solution, even at the very high concentrations—several moles per liter—at which the Raman spectra were determined. If any undissociated component is present, its concentration is too low to be detected in the spectrum.

A more detailed analysis of the spectra of the various molecular types studied may now be attempted.

1. Molecules of the "diatomic" type

The simplest type of molecule studied consists of two relatively heavy atoms linked together,

with one or more hydrogen atoms attached to each. The methyl ammonium ion, the hydrazine di-ion, and the hydroxyl ammonium ion are typical examples. All these molecules, like ethane, show a powerful Raman line near 1000 cm^{-1} which corresponds to a valence vibration of the two heavy atoms. Such a system may be treated approximately as if it were diatomic, on the basis of the assumptions outlined above. The force constant f in dynes per cm, is given directly by the formula $Q\nu^2 = f/\mu$ where μ, the reduced mass, is expressed in atomic weight units (oxygen = 16), ν is the observed frequency expressed in cm^{-1}, and the constant Q has the value 0.0586.[14, 12] In Table I, the force constants calculated by this method are given for six different molecules or ions of this type.

The strongest bond found among these compounds is the $^+N-N^+$ bond in the doubly charged hydrazinium ion. The order of diminishing force constants is: $f(^+N-N^+) > f(C-N) > f(C-N^+) > f(C-C)$; while $f(C-O)$ and $f(^+N-O)$ are nearly equal to each other and to $f(C-N)$.

The assignment of the valence vibration in $^+H_3N \cdot NH_2$ and $H_2N \cdot NH_2$ is slightly uncertain. Both these substances show a strong line near 1100 cm^{-1}; we have tentatively followed Kohlrausch[7] in regarding this as arising from the deformation vibration of the $-NH_2$ group, and in taking the valence vibration of the N—N linkage as the line given in Table I. If this is correct, there is a remarkable decrease in the force constant of the bond with decreasing charge on the nitrogen atoms: $f(^+N-N^+) > f(^+N-N) > f(N-N)$.

2. Dimethyl amine ($CH_3 \cdot NH \cdot CH_3$) and the dimethyl ammonium ion ($CH_3 \cdot {}^+NH_2 \cdot CH_3$)

These compounds may be approximately treated as symmetrical, bent triatomic structures, exactly analogous to propane, and resembling such simple molecules as water or sulfur dioxide. Such a triatomic structure should give rise to three fundamental frequencies: one corresponding to a symmetrical deformation of the molecule (ν_2) and two valence vibrations, one symmetrical (ν_1) and one asymmetrical (ν_3). All these frequencies should be present in the Raman spectrum, the asymmetrical vibration being depolarized ($\rho = 6/7$), the other two polarized ($\rho < 6/7$).[15, 16]

The dimethyl ammonium ion shows three strong Raman lines in the region below 1050 cm^{-1}: at 412, 895 and 1029. (There are only two other, much weaker lines between 1050 and 1450 cm^{-1}.) These three frequencies may, therefore, probably be taken as corresponding to the three fundamental vibrations. Polarization measurements show the lines at 412 and 895 to be strongly polarized, while that at 1029 is almost completely depolarized, and may, therefore, be taken as representing the asymmetrical valence

TABLE II. *Bond force constants and valence angles in certain ions and molecules.*

1. Molecules with three groups (valence force treatment).

Frequency and Polarization		$CH_2 \cdot CH_2 \cdot CH_3$	$CH_3 \cdot NH \cdot CH_3$	$CH_3 \cdot {}^+NH_2 \cdot CH_3$
ν_1	P	867(8)	931(4)	895(4)
ν_2	P	373(1*b*)	390(1)	412(2)
ν_3	D	1053(3*b*)	1078(0)	1029(2)
Valence Angle α		116°8′	114°28′	115°50′
Force Constant f in dyne/cm		3.84×10^5	4.24×10^5	4.08×10^5
Deformation Constant d		0.336×10^5	0.318×10^5	0.449×10^5

2. Pyramidal molecules with four groups (valence force treatment).

Frequency and Polarization		$(CH_3)_3CH$	$(CH_3)_3N$	$(CH_3)_3NH^+$
ν_1	P	794(9)	827(5)	821(5)
ν_2	P	438(1)	365(2)	468($\frac{1}{2}$)
ν_3	D	962(4*b*)	1036(2*b*)	987(4)
ν_4	D	370(4*b*)	423(3)	406(1)
Valence Angle α		116°20′	109°25′	117°0′
f from ν_1 and ν_2		Imaginary	4.13×10^5	Imaginary
f from ν_3 and ν_4		3.20×10^5	3.46×10^5	3.62×10^5
d from ν_3 and ν_4		0.75×10^5	0.48×10^5	0.52×10^5

3. The tetramethyl ammonium ion $(CH_3)_4N^+$.* (Employing treatment of Urey and Bradley.)[*]

ν_1 (totally symmetric): 752(6)	Force Constant $K_1 = 2.18 \times 10^5$
ν_2 (doubly degenerate): 372(2)	Deformation Constant $K_2 = 0.43 \times 10^5$
ν_3 (triply degenerate): 955(6)	Repulsion Constant $\gamma_2 = 0.35 \times 10^5$
ν_4 (triply degenerate): 455(2)	ν_3 (calculated) = 904 cm^{-1} ν_4 (calculated) = 511 cm^{-1}

* In this treatment, it was assumed that $n = 7$; that is, that the repulsive potential between the corner methyl groups varies as the inverse seventh power of the distance between them. For the precise definition of the constant γ_2, see the paper of Urey and Bradley. Kohlrausch and Köppl[3] have calculated K_1 for tetramethyl methane as 2.03×10^5, using the same treatment.

[14] Q is $(4\pi^2c^2)/N$, where c is the velocity of light and N is Avogadro's number.

[15] G. Placzek, *Handbuch der Radiologie* (Leipzig, 1934), p. 205.

[16] E. B. Wilson, Jr., J. Chem. Phys. **2**, 432 (1934).

vibration (ν_3). Of the other two lines, 412, being much lower in frequency and much less intense than 895, may be taken as the deformation frequency (ν_2) and 895 as the symmetrical valence oscillation (ν_1).

Dimethyl amine shows three corresponding lines at 415, 930 and 1082; and propane[3] at 373, 867 and 1053. Although no polarization measurements appear to have been made on either of these compounds, there seems little doubt, on the basis of the relative frequencies and intensities, that the assignment of frequencies should correspond to that made for the dimethyl ammonium ion. Kohlrausch[7] has already assumed such an assignment and has calculated the configuration and force constants of the propane and dimethyl amine molecules, employing the assumptions of a valence force system.[17] The results of his calculations, and of our own on the dimethyl ammonium ion utilizing the same treatment, are given in Table II. The values of the valence angle α are all somewhat larger than the tetrahedral angle (109°28′), but are physically not unreasonable. The values of the force constant f again follow the order $f(C-N) > f(C-N) > f(C-C)$, as in the "diatomic" molecules listed in Table I; but the absolute values of f in all cases are markedly lower than for the corresponding linkages in the "diatomic" molecules.

On the whole, the equations for a valence force system give reasonable estimates for the configuration and interatomic forces in a system such as the dimethyl ammonium ion. The exact physical significance of the molecular constants so calculated may not be altogether certain, but they are useful in making comparisons between molecules of closely related type.

3. Ethyl amine ($CH_3CH_2NH_2$) and the ethyl ammonium ion ($CH_3CH_2NH_3^+$)

These substances are very similar in structure to those just discussed. The ethyl ammonium ion,[8] indeed, shows three powerful Raman lines, at 411, 873 and 1047 cm^{-1}, corresponding very closely in position and relative intensity to the three fundamental frequencies of its isomer, the dimethyl ammonium ion, or of propane. It may be inferred that the geometrical pattern and the interatomic force constants in the three substances are not dissimilar. It should be noted, however, that the ethyl ammonium ion corresponds in structure to an *unsymmetrical* triatomic molecule. According to the calculations of Wilson,[16] all three fundamental vibrations should, therefore, give rise to polarized Raman lines ($\rho < 6/7$) in the spectrum of a molecule of this sort. The exact polarization studies necessary to verify this prediction have not yet been undertaken, but it would be of interest to determine how far the relatively slight degree of asymmetry produced by the difference between the CH_3 and the NH_3^+ group could be detected by such measurements.

The spectrum of ethyl amine, in the region from 1000 to 1400 cm^{-1}, is extraordinarily rich in lines, showing far greater complexity than the ethyl ammonium ion. Part of this complexity may be due to the very favorable conditions of the exposure: the substance was present in very high concentration (10.7 mole/liter, in water) and the spectrum was almost completely free from fluorescence or background of any sort. Hence relatively faint lines, which might otherwise have been missed, were clearly revealed. Nevertheless, the difference in spectrum between the free amine and the ion seems to point to a greater complexity in the configuration of the former. This may be due to the greater dissymmetry of the $-NH_2$ group than of the $-CH_3$ or $-NH_3^+$ group. Each of the two latter groups possesses a threefold axis of symmetry (which coincides with the direction of the fourth valence bond in the C or N^+ atom), while the twofold symmetry axis of the $-NH_2$ group does not lie in the direction of the third nitrogen valence bond. Therefore, rotation of the $-NH_2$ group around the axis of the C–N bond in ethyl amine can give rise to more different molecular configurations than can a similar rotation of a $-CH_3$ or NH_3^+ group. Whether this conception is relevant to the observed character of the spectrum of ethyl amine cannot yet be definitely decided, but it appears a possible explanation.

4. The *n*-propyl ammonium ion ($CH_3CH_2CH_2NH_3^+$) (not shown in Fig. 1)

This is analogous to *n*-butane, and the two compounds show very similar spectra. Kohlrausch

[17] F. Lechner, Ber. Wiener Akad. Wiss. IIa **141**, 291, 633 (1932). See also W. G. Penney and G. B. B. M. Sutherland, Proc. Roy. Soc. **156A**, 654 (1936).

and Köppl[3] have considered *n*-butane in terms of a valence force treatment and concluded that the hydrocarbon chain must exist in at least two different configurations, in order to account for all the observed frequencies. A similar treatment might well prove applicable to the propyl ammonium ion but has not yet been carried out.

5. Trimethyl amine ($(CH_3)_3N$) and the trimethyl ammonium ion ($(CH_3)_3NH^+$)

These molecules may be considered as trigonal pyramids, with a symmetrical base, similar to ammonia in configuration, and exactly analogous to isobutane, $(CH_3)_3CH$. Such a system gives rise to four fundamental frequencies: a symmetrical valence pulsation (ν_1), a symmetrical deformation (ν_2), and two doubly degenerate vibrations (ν_3 and ν_4).[15, 16] All four should be present in the Raman spectrum, ν_1 and ν_2 being polarized, ν_3 and ν_4 depolarized.

The trimethyl ammonium ion shows four Raman frequencies below 1050 cm^{-1}: those at 468 and 821 are strongly polarized, those at 406 and 987 are almost completely depolarized. 821 is distinguished by its high intensity; it almost certainly represents the frequency ν_1, and 468 is, therefore, ν_2, while 987 and 406 represent the two doubly degenerate frequencies, ν_3 and ν_4.

Lechner[17] has derived the equations for a valence force system as applied to a molecule of this type. From his equations, the valence angle (that is, the angle between the threefold axis of symmetry and any one of the three $C-N^+$ bonds) is determined by the ratio $(\nu_3\nu_4)/(\nu_1\nu_2)$. Numerical calculation gives this angle for the trimethyl ammonium ion as 117°0′, much larger than the tetrahedral angle. Such a value is highly improbable; any deviation from the tetrahedral angle would be expected to be in the opposite direction, owing to repulsion between the methyl groups. This result shows the inadequacy of the valence force system as an actual picture of the intramolecular potential energy field in a molecule of this sort; an inadequacy already pointed out by Kohlrausch and Köppl.[3]

The spectrum of isobutane[3, 4] is exactly analogous to that of the trimethyl ammonium ion, showing the four fundamental frequencies, 437 and 795 (both polarized), and 370 and 965 (both depolarized). The calculated value for the valence angle, assuming a valence force system, is 116°20′, almost identical with that for the trimethyl ammonium ion. Further details regarding these two molecules are given in Table II, along with Kohlrausch's calculations on trimethyl amine.[18]

The spectrum of trimethyl amine is appreciably different. There is a broad diffuse band near 270 cm^{-1} which Ananthakrishnan[6] has found to be depolarized. Above this are four lines in the region below 1050 cm^{-1}: 365 and 827 (polarized) and 423 and 1036 (depolarized).[19] Both Ananthakrishnan and Kohlrausch[7] have taken these as the four fundamentals, and the latter has calculated the molecular force constants and valence angle, employing a valence force system, his assignment of the frequencies being confirmed by Ananthakrishnan's polarization measurements (Table II).

It will be noted that in this case it is the lowest of the four fundamental frequencies which is polarized, while the one just above it is depolarized; the opposite relation is found in isobutane and the trimethyl ammonium ion. This difference illustrates the need for caution in assigning frequencies to modes of vibration, when comparison is made between analogous compounds. Also it shows again that the substituted ammonium ion is much closer in spectral type to the corresponding hydrocarbon than to the corresponding amine. The broad band at 270 in trimethyl amine, moreover, has no analog in either of the other compounds. The possibility remains that it represents one of the fundamental vibrations, and that the assignment of the other frequencies requires revision.

6. The tetramethyl ammonium ion ($(CH_3)_4N^+$)

On the basis of stereochemical evidence, this ion represents a symmetrical tetrahedral structure, exactly analogous to tetramethyl methane, $(CH_3)_4C$. Such a system should give rise to four fundamental frequencies: one totally symmet-

[18] If the assignment of the frequencies 406 and 468 in the trimethyl ammonium ion be interchanged, the calculated valence angle assumes the much more plausible value, 110°30′; similarly interchanging the assignment of the frequencies 370 and 437 in isobutane gives a valence angle of 109°50′. Such an assignment of the frequencies in isobutane was originally made by Kohlrausch and Köppl,[3] but it appears irreconcilable with the polarization measurements.

[19] The line at 365 was not observed in our studies, probably owing to strong continuous background in this region. Both Kohlrausch and Ananthakrishnan have reported it.

TABLE III. *Bond force constants (f), for certain linkages in two different types of molecules.*

(1) BOND	(2) METHYL DERIVATIVE	(3) f METHYL $\times 10^{-5}$	(4) TETRAHEDRAL DERIVATIVE	(5) f TET $\times 10^{5}$ U. & B.	(6) f TET $\times 10^{5}$ VALENCE FORCE
C−C	H_3C-CH_3	4.31	$C(CH_3)_4$	2.03	4.70
C−N$^+$	$H_3C-{}^+NH_3$	4.63	$^+N(CH_3)_4$	2.18	4.97
C−Cl	H_3C-Cl	3.12	CCl_4	1.74	4.35
C−Br	H_3C-Br	2.61	CBr_4	1.40	3.30

The third column gives the force constant of each bond calculated as for a "diatomic" molecule. The first two values are from Table I, the last two from reference 12, p. 154. The fifth column gives f as calculated for the tetrahedral derivative by the method of Urey and Bradley.[22] The last column gives f as calculated for the same compound by a simple valence force treatment.[21] The value of f so obtained is much higher, but does not fit the observed data nearly so well as the method of Urey and Bradley.

rical pulsation, ν_1, which should be completely polarized ($\rho=0$); one doubly degenerate vibration, ν_2; and two triply degenerate vibrations, ν_3 and ν_4. All the last three frequencies should be completely depolarized ($\rho=6/7$). Observation shows four frequencies below 1000 cm^{-1}: at 372, 455, 752, and 955, the two latter being very intense. Somewhat weaker lines at 1047, 1173 and 1289 are also present: it seems probable, however, that these are not fundamentals of the C−N skeleton. They may represent deformation frequencies involving the C−H linkages in the methyl groups;[20] and we shall take the four lowest frequencies as representing the fundamental vibrations. Of these, all are nearly depolarized with the exception of 752 cm^{-1}, which is almost completely polarized, being comparable in this respect (as a comparison photograph showed) with the frequency 459 cm^{-1} in carbon tetrachloride.

There is, therefore, no doubt that the line at 752 corresponds to the totally symmetric vibration, ν_1. A tentative assignment of the other frequencies may be made with the aid of calculations on a suitable type of molecular model. The equations for a valence force system[21] are quite inadequate for the description of this system; but the treatment of Urey and Bradley[22] for pentatomic tetrahedral molecules gives a much better approximation. These authors assume, in addition to forces resisting the stretching or bending of the valence bonds, that repulsive forces are present between the atoms at the corners of the tetrahedron, which vary as a high inverse power of the distance between them. Using the equations derived by Urey and Bradley, we have calculated the characteristic force constants for the tetramethyl ammonium ion from the observed frequencies. The most reasonable values were obtained by taking the lowest observed frequency (372 cm^{-1}) as ν_2, the doubly degenerate frequency. The values of the interatomic force constants, and of the frequencies, ν_3 and ν_4, as calculated on this basis, are given in Table II.

The calculated values of ν_3 and ν_4 show distinct discrepancies from the observed values. ν_3 as calculated is too low by about 6 percent; ν_4 too high by about 11 percent. For simple molecules like CCl_4, on the other hand, Urey and Bradley found agreement within 1 or 2 percent. The discrepancy in our case, however, is not surprising, since we have made the rather gross approximation of treating the methyl groups as if they were single atoms.

The value of the stretching force constant f, for the C−N$^+$ bond, is only 2.18×10^5 according to these calculations, as compared with 4.63×10^5 in the methyl ammonium ion (Table I). Similarly Kohlrausch and Köppl[3] have calculated f(C−C) in tetramethyl methane as 2.03×10^5 by the method of Urey and Bradley, while in ethane (Table I) f(C−C) is 4.31×10^5. The apparent bond strength changes by more than a factor of two in each case. A similar divergence is found when f, as calculated by Urey and Bradley for the C−Cl or C−Br bond (in CCl_4 or CBr_4), is compared with f(C halogen) in CH_3Cl or CH_3Br (calculated for these molecules, employing the simple "diatomic" treatment. See Table III). Whether these wide differences represent a real change in bond strength, or whether they are simply a result of the employment of different potential functions in the two types of calculation, is a question that must, for the present, be left open.

[20] T. F. Anderson, J. Chem. Phys. **4**, 161 (1936), has considered the possibility that resonance may occur between the fundamental frequencies in molecules of this type, leading to the production of additional lines in the spectrum, which are actually found in certain cases. It is possible that one or two of the lines observed by us are due to this, but we have not undertaken detailed calculations to test this hypothesis.

[21] F. Lechner, Akad. Anzeiger d. Wien. Akad. der. Wiss. No. 14 (1933).

[22] H. C. Urey and C. A. Bradley, Phys. Rev. **38**, 1969 (1931).

7. The trimethyl hydroxyl ammonium ion $(CH_3)_3N^+ \cdot OH$

This is the cation of trimethyl amine oxide hydrochloride; in electronic configuration, it is the exact analogue of tertiary butyl alcohol, $(CH_3)_3COH$;[23] and the Raman spectra of the two substances are strikingly alike. Even more significant in connection with the present investigation, however, is its relation to the tetramethyl ammonium ion, from which it differs in the replacement of one methyl by a hydroxyl group. In spite of this change, it shows four Raman lines below 1000 cm^{-1} at 382, 500, 754 and 947—which are almost identical in frequency and relative intensity with the four fundamentals of the tetramethylammonium ion (372, 455, 752 and 955). The disturbance of molecular symmetry produced by the substitution of the hydroxyl for a methyl group is apparently very slight, since there is scarcely any sign of a splitting of the doubly or triply degenerate frequencies, such as might be expected to result from a decrease in the symmetry of the ion. There is, indeed, one slight change: the line at 500 in $(CH_3)_3{}^+N \cdot OH$ is shifted to a higher frequency, and is much broader, than the line at 455 in $(CH_3)_4N^+$. This may represent an incipient splitting of this (presumably triply degenerate) frequency, which could perhaps be resolved into component lines in a spectrograph of higher dispersion. Tertiary butyl alcohol actually does show a doubling of the corresponding frequency, giving two weak lines at 454 and 471, while tetramethyl methane shows one corresponding line at 429.

Rank and Bordner[24] have found that the substitution of a single deuterium atom for hydrogen, in one of the methyl groups in tetramethyl methane, leads to the appearance of several new frequencies, due at least in part to the removal of vibrational degeneracy by reduction in molecular symmetry. Such a change would appear to be much slighter than that involved in the substitution of a hydroxyl for a methyl group; yet the actual perturbation of molecular symmetry produced is apparently greater. The results show that a hydroxyl and a methyl group are, to a remarkable degree, equivalent as components of a vibrating molecular system. (Compare discussion in reference 23.)

[23] A. Dadieu, A. Pongratz and K. W. F. Kohlrausch, Monatsh. Chemie **61**, 369 (1932); Ber. Wiener Akad. (IIa) **141**, 267 (1932).

[24] D. H. Rank and E. R. Bordner, J. Chem. Phys. **3**, 248 (1935).

The Dissociation of the Hydrazinium Ion in Relation to its Raman Spectrum

The interpretation of the spectrum of hydrazine dihydrochloride requires some additional discussion. The line at 1036 cm^{-1}, which has been taken as representing the valence vibration of the $^+N-N^+$ linkage, is very sharp and extremely intense. It is flanked by two much weaker and broader lines, one at 968 and one at 1110 cm^{-1}. These, however, are probably not due at all to the ion $^+H_3N \cdot NH_3^+$, but to $^+H_3N \cdot NH_2$ which arises from it by dissociation; for these same lines are present, in much higher intensity, in the spectrum of the monohydrochloride, $H_2N \cdot NH_3{}^+Cl^-$, which shows no trace of the line at 1036.

$^+H_3N-NH_3^+$ is known to be a very strong acid, largely dissociating to $^+H_3N \cdot NH_2$. Recently Schwarzenbach[25] has estimated its dissociation constant, $K=(H^+)(^+H_3N \cdot NH_2)/(^+H_3N \cdot NH_3^+)$, as being not far from 7.6, according to his e.m.f. measurements on the hydrogen electrode. Thus, even at the high acidity employed in our measurements (normal HCl added to approximately 2 molar hydrazine dihydrochloride), a large proportion of the doubly charged ion should dissociate to give the monoion. The concentration ratio of the two forms cannot be exactly calculated without further knowledge of the activity coefficients of the ions. The intensity of the 1036 line in the Raman spectrum, however, compared with those at 968 and 1110, indicates that both ions are present in significant amounts, but that the $^+H_3N \cdot NH_3^+$ ion predominates. This result is roughly what might be expected from Schwarzenbach's electrometric measurements. It supplies approximate confirmation, by an entirely independent method, of his estimate of the order of magnitude of the dissociation constant. Accurate measurements of the relative intensity of the different Raman lines at varying hydrogen ion concentrations might well prove a very powerful

[25] G. Schwarzenbach, Helv. Chim. Acta **19**, 178 (1936). For an earlier estimate, see Kolthoff, J. Am. Chem. Soc. **46**, 2009 (1924), and also Gilbert, J. Am. Chem. Soc. **46**, 2648 (1924).

tool for the determination of this and other dissociation constants.[26]

The second dissociation constant of the hydrazinium ion, $K_2=(H^+)(H_2N^-NH_2)/(H_3{}^+N\cdot NH_2)$, is $10^{-8.1}$ from Schwarzenbach's measurements. As the Raman spectrum of the monohydrochloride was determined at *p*H 6.3, the amount of $H_2N\cdot NH_2$ should thus be less than one fiftieth of the total hydrazine present, and it may safely be assumed that, in this case, the observed spectrum arises only from the $^+H_3N\cdot NH_2$ ion.

Raman Frequencies Involving the C—H and N—H Linkages

Fig. 1 shows that among the compounds studied, only those containing an un-ionized $^-NH_2$ or ^-NH group give rise to Raman lines in the region 3300–3400. The primary amines give two lines, one near 3320 which is very strong, and another weaker one near 3380. Cabannes and Rousset[27] have shown that in methyl amine, the former is highly polarized, and the latter presumably depolarized; hence they must correspond respectively to the symmetrical and asymmetrical valence oscillations of the $^-NH_2$ group. Kohlrausch[7] has suggested that the third (deformation) frequency of this group lies near 1100 cm^{-1}. Dimethyl amine, with an ^-NH group, shows but one line between 3300 and 3400, as might be expected.

Positively charged $-NH_3{}^+$, $-NH_2{}^+$, or $-NH^+$ groups appear to give rise to no Raman lines above 3300 cm^{-1}. This difference represents probably the most striking contrast in the spectra of the amines and of the corresponding ammonium ions. The unsubstituted $NH_4{}^+$ ion, however, has been reported by several observers to show two or three relatively broad and faint Raman lines[28] between 2900 and 3250 cm^{-1}. Similarly, the hydroxyl ammonium ion gives rise to very broad lines at 2741, 2953 and 3200; these are probably due to the N—H linkages, except for the last which may arise from an —OH vibration. The methyl ammonium ion gives four strong Raman lines between 2800 and 3050. At least two—possibly three—of these lines must arise from the internal vibrations of the $-CH_3$ group; the other one, or two, from the $^+NH_3$ group. For reasons pointed out below, the two lines of higher frequency (2975 and 3032) are probably to be assigned to the $-CH_3$ group, and thence by exclusion the other two, rather weaker lines, 2833 and 2914, may tentatively be attributed to the $-NH_3{}^+$ group. In general, it would appear that the lines due to the $-NH_3{}^+$ group are broader, fainter and of decidedly lower frequency than those due to the $-NH_2$ group.

The $CH_3NH_3{}^+$, $^+NH_3OH$ and $C_2H_5NH_3{}^+$ ions all show a line of moderate intensity between 1200 and 1270 cm^{-1}. This may correspond to a deformation frequency of the $NH_3{}^+$ group.

All the methylated ammonium ions, from the monomethyl to the tetramethyl derivative, show two strong lines, one at 2980($\pm$10) and the other at 3040($\pm$10). In every case, the 2980 line is found to be almost completely polarized (Table V), while the 3040 line is almost completely depolarized. The constancy of the frequencies and of the relative polarizations of these two lines suggests that they arise from the same modes of vibration in all these compounds. If this is true, they must be associated with the $-CH_3$ group, not with the ^+N-H linkage, since both lines are found in high intensity in the $(CH_3)_4N^+$ ion, which contains no N—H bond. One, perhaps, represents a symmetric and the other an antisymmetric oscillation of the $-CH_3$ group. It is curious, however, that the intensity of 3040, relative to that of 2980, increases progressively with the number of methyl groups in the molecule. In the $CH_3NH_3{}^+$ ion, 2980 is roughly twice as intense as 3040; in the $(CH_3)_4N^+$ ion, this relation is reversed. The presence of the line at 3040 is confined to one group of compounds: namely, the substituted ammonium ions which possess at least one methyl group directly attached to the positively charged nitrogen atom. The hydrocarbons, the uncharged amines, and the ammonium ions which have only a methylene ($-CH_2$) group adjacent to the charged nitrogen (for instance, the ethyl- or *n*-propyl ammonium

[26] A study of hydrazine dihydrochloride in 20 percent aqueous solution without excess HCl showed that the intensity of the 1036 line was markedly reduced as compared with that of the lines at 968 and 1110. This is what should have been expected, since the dissociation of $^+H_3N\cdot NH_3{}^+$ to $^+H_3N\cdot NH_2$ will be markedly greater at the lower hydrogen ion concentration.

[27] J. Cabannes and A. Rousset, Ann. de. physique **19**, 270 (1933).

[28] I. R. Rao and C. S. Rao, Zeits. f. Physik **88**, 127 (1934); A. C. Menzies and H. R. Mills, Proc. Roy. Soc. **A148**, 407 (1935); R. Ananthakrishnan, Nature **138**, 803 (1936).

ions) show no line in this range with a frequency higher than 2990 cm^{-1}.

Raman Spectrum and Hydration of Amines

The spectra of all the amines studied in this investigation were obtained in aqueous solution. On the other hand, the recent observations of Kohlrausch[7] and of Ananthakrishnan[6] were made on anhydrous amines. Comparison of the two sets of data should, therefore, reveal the effects of hydration on the amino group. The chief differences found are in the frequencies between 2700 and 3000 cm^{-1}, which run fairly consistently 20 or 30 wave numbers higher in the hydrated than in the anhydrous amines. This difference might possibly be due to a small systematic error either in Kohlrausch's investigation or in ours. Probably, however, there is no such error, since the earlier determinations of Dadieu and Kohlrausch[29] on methyl amine and ethyl amine in water give results which are very closely concordant with our own determinations under the same conditions.

The N−H frequencies, between 3300 and 3400, are virtually unaffected by solution in water. The same is true of the fundamental frequencies of the heavy molecular skeleton, lying below 1100 cm^{-1}. The very slight shifts observed are virtually all within the experimental error. We have indeed found a few relatively weak lines between 1100 and 1300 cm^{-1}, not reported by Kohlrausch; but this is probably due to the high intensity and exceptional clarity of our own exposures, rather than to any intrinsic difference between the hydrated and the unhydrated amines.

Altogether the effects of hydration are remarkably slight. This is especially surprising since Moore and Winmill[30] concluded from a painstaking analysis of the conductivity of amines, and their distribution coefficients between different solvents, that the reaction

$$NR_3+H_2O \rightleftharpoons NR_3HOH$$

(R = H or an alkyl radical)

proceeds largely in the direction of the hydrated form. For instance, they estimate that methyl amine in water should exist to the extent of over 90 percent in water as CH_3NH_3OH, the nitrogen and oxygen being coupled by what is generally known today as a hydrogen bond. Certainly one might expect the fundamental vibrations of the system, CH_3NH_3OH, to be very different from those of CH_3NH_2; yet no such difference is in fact observed. If the conclusions of Moore and Winmill are valid, then, we must assume that the linkage involved in the hydrogen bond is so loose that the two parts of the molecule thus joined continue to vibrate almost as if they were completely independent of each other.

Characteristic Frequencies of the Amino Group and the Dipolar Ionic Structure of the Amino Acids

Solutions of the sodium salts of glycine and alanine show a strong Raman frequency near 3320 cm^{-1}, and indications of a weaker line near 3380. These lines are characteristic of the unionized amino group. The free amino acids, however (see reference 8), show no evidence of any Raman frequencies above 3030, although their spectra are clearer and show much less continuous background than those of the sodium salts. By comparison with the spectra of the amines and their hydrochlorides, this indicates that the amino group in the isoelectric amino acids carries a positive charge, and that, therefore, these molecules exist as dipolar ions (or zwitterions), $^+H_3NRCOO^-$. This supplements the earlier spectroscopic proof of this structure,[8] based on studies of the ionization of the carboxyl group. The same conclusion has been reached independently by Freymann, Freymann and Rumpf[31] who have studied the infrared absorption band near 1.04μ, characteristic of the uncharged amino group (presumably the second harmonic of the band near 3300 cm^{-1}). They have shown that this vanishes when the nitrogen atom acquires a fourth covalency, as in the ammonium ions, and is likewise absent in glycine and taurine, although present in their sodium salts. From this, they deduce the dipolar ionic structure of glycine and taurine. The study of Raman and infrared spectra was scarcely re-

[29] A. Dadieu and K. W. F. Kohlrausch, Monatsh. Chemie **55**, 379 (1930); **57** 225 (1931).

[30] T. S. Moore and T. F. Winmill, J. Chem. Soc. **91**, 1373 (1907); **101**, 1635 (1912). See also Sidgwick, reference 2, p. 97.

[31] M. Freymann, R. Freymann and P. Rumpf, J. de. phys. et rad. [7] **7**, 30 (1936).

quired to establish the validity of this structure, which is supported by many other lines of evidence;[32] but these spectroscopic methods furnish with great clarity and simplicity important information concerning structure. For other related compounds whose structure is still in doubt, such methods should prove of the greatest value in reaching a decision between alternative possible structures.

I am greatly indebted to Mr. Joseph Shack for his constant and valuable assistance in the experimental work; also to Professor E. B. Wilson, Jr., for helpful discussions and particularly for his suggestions regarding the use of Polaroid in making the polarization studies reported in Table V.

TABLE IV. *Complete list of observed Raman spectra.*

The method of notation for the spectra is the same as that previously employed (reference 8, Table IV). A number of the substances here studied have been previously observed, as follows:

Hydroxyl amine and hydrazine hydrochlorides: Ananthakrishnan,[6] Freymann, Freymann and Rumpf.[31]

Methyl alcohol: see the extensive references in J. H. Hibben, Chem. Rev. **18**, 1 (1936); or J. Weiler, in Landolt-Börnstein's *Tabellen* fifth edition, 3rd Ergänzungsband, Part II.

Methyl, ethyl, dimethyl and trimethyl amines: Kohlrausch.[7] For trimethyl amine, see also Ananthakrishnan.[6] Both these papers give references to the earlier literature on amines.

1. *Hydrazine dihydrochloride*, $Cl^- {}^+H_3N \cdot NH_3{}^+Cl^-$, 22 percent aqueous solution +1 normal HCl to repress dissociation of H^+ ion. $\Delta\nu$=968 (1*b*) (*k*, *e*); 1036 (5) (very sharp) (*k*, *i*, *e*); 1110 (½*vb*) (*k*, *e*); 1645 (2*vb*) (*e*); 2655 (0) (*k*); 3187 (3*vb*) (*k*).

The lines at 968 and 1110 probably arise from the ion $^+H_3N \cdot NH_2$. The reasons for this assignment are discussed in the text.

2. *Hydrazine monohydrochloride*, $^-Cl\ H_3N^+ \cdot NH_2$, 25 percent in water (prepared from the dihydrochloride by addition of one equivalent of C.P. NaOH. Final *p*H 6.3±0.2. Due to method of preparation, solution contains NaCl, about 2.3 molal). $\Delta\nu$=965 (4) (*k*, *e*); 1109 (2) (*k*, *e*); 1274 (½*vb*) (*k*, *e*); 1419 (1) (*k*, *e*); 1530 (½) (*e*); 1630 (3*vb*) (*k*, *e*); 2692 (0) (*k*); 2983 (2*b*) (*k*); 3219 (3) (*k*); 3309 (1) (*k*).

The spectra of both the hydrochlorides of hydrazine show a diffuse darkening of the plate in the region from 0 to about 700 cm^{-1}, on the long wave-length side of both the *k* and *e* mercury lines, with broad maxima of intensity near 600 cm^{-1}.

The broad line at 1630 (or 1645) is far stronger than the water band in the same range, and must presumably be attributed to the hydrazine ions, rather than to water.

3. *Hydroxylamine hydrochloride*, $Cl^- {}^+NH_3OH$ (Eastman m.p. 150–152°), 40 percent aqueous solution, +0.2*N* HCl. $\Delta\nu$=1006 (6, very sharp) (*k*, *i*, *e*); 1205 (1*vb*) (*k*, *e*); 1533 (1*vb*) (*k*, *e*); 1625 (1*vb*) (*k*, *e*) (water); 2741 (2*vb*) (*k*); 2953 (4*vb*) (*k*, *e*); 3200 (2*b*) (*k*).

All the lines in this spectrum, except 1006, are extremely broad and diffuse.

4. *Methyl alcohol*, CH_3OH (Baker's C.P. analyzed, dried over sodium sulfate and distilled).

$\Delta\nu$=1032 (6) (*k*, *i*, *e*); 1114 (1*b*) (*k*, *e*); 1163 (1) (*k*, *e*); 1461 (5*vb*) (*k*, *e*); 2589 (1*vb*) (*k*); 2839 (7*b*) (*k*, *i*, *e*); 2945 (6*b*) (*k*, *i*, *e*); 3390±200 (3, band) (*k*, *e*). The line at 2589 has not previously been reported.

5. *Methyl alcohol* (30 percent in water).

$\Delta\nu$=1020 (6) (*k*, *i*, *e*); 1115 (1) (*k*, *e*); 1162 (½) (*k*); 1466 (5*b*) (*k*, *e*); 2604 (1*vb*) (*k*); 2846 (6*b*) (*k*, *i*, *e*); 2949 (6) (*k*, *i*, *e*). [Band near 3400 coincides with water band.]

6. *Methyl amine*, CH_3NH_2, in water (10.3 moles per liter, by titration). Prepared by distillation of the purified hydrochloride to which NaOH had been added.

$\Delta\nu$=1034 (7) (*k*, *i*, *f*, *e*); 1110 (0) (*e*); 1174 (½*b*) (*k*, *e*); 1428 (½*b*) (*k*); 1474 (4*b*) (*k*, *e*); 1614 (2*b*) (*k*, *e*); 2822 (6) (*k*, *e*); 2904 (6) (*k*, *i*, *e*); 2964 (6) (*k*, *i*, *e*); 3322 (6) (*k*, *i*, *e*); 3382 (2) (*k*, *e*).

For the Raman spectrum of methyl amine hydrochloride, see reference 8.

7. *Ethyl amine*, $CH_3CH_2NH_2$, in water (10.7 moles per liter by titration). Distilled from recrystallized ethyl amine hydrochloride, to which excess NaOH had been added.

$\Delta\nu$=427 (4*b*) (*k*, *i*, *e*); 882 (8*b*) (*k*, *i*, *g*, *f*, *e*); 1009 (½) (*k*, *e*); 1045 (3) (*k*, *e*); 1081 (4) (*k*, *e*); 1135 (3*b*) (*k*, *e*); 1202 (1) (*k*, ?); 1250 (1*b*) (*k*, *e*); 1300 (1) (*k*, *e*); 1367 (1) (*k*, *e*); 1457 (8*vb*) (*k*, *e*); 1482 (1) (*k*); 1585 (0*vb*) (*k*, *e*); 2691 (1) (*k*); 2727 (3) (*k*); 2780 (3) (*k*); 2877 (10*b*) (*k*, *i*, *e*); 2932 (10*b*) (*k*, *i*, *e*); 2977 (10*b*) (*k*, *i*, *e*); 3308 (10*vb*) (*k*, *i*, *e*); 3372 (4*b*) (*k*, *i*); 3678 (1*b*) (*k*).

For the Raman spectrum of ethyl amine hydrochloride, see reference 8.

8. *n-Propyl amine hydrochloride*, $CH_3CH_2CH_2NH_3{}^+Cl^-$, 40 percent solution in water, +0.5*N* HCl. (Hoffman-La Roche product.)

$\Delta\nu$=458 (1) (*k*, *e*); 833 (2) (*k*, *e*); 870 (3) (*k*, *e*); 955 (1) (*k*, *e*); 1050 (3) (*k*, *i*, *e*); 1192 (¼) (*e*); 1298 (1) (*k*, *e*); 1333 (1) (*k*, *e*); 1455 (4) (*k*, *e*); 1531 (*e*, ?); 1644 (0*vb*) (*e*) (water); 2667 (1) (*k*); 2771 (1) (*k*); 2887 (4) (*k*, *e*); 2940 (6) (*k*, *i*, *e*); 2983 (4) (*k*, *e*).

9. *Dimethyl amine*, $(CH_3)_2NH$, in water (4.4 moles per liter, by titration). Distilled from recrystallized dimethyl amine hydrochloride and NaOH into Raman tube.

$\Delta\nu$=415 (3) (*e*); 930 (5) (*k*, *i*, *f*, *e*); 1082 (3) (*k*, *e*); 1137 (2) (*k*, *i*, *e*); 1189 (2) (*k*, *e*); 1243 (2) (*k*, *e*); 1412 (1) (*k*); 1450 (4*b*) (*k*, *e*); 1479 (6) (*k*, *e*); 1657 (½*vb*) (*e*) (water ?); 2803 (8*b*) (*k*, *i*); 2847 (6) (*k*, *e*); 2906 (5*vb*) (*k*, *i*, *e*); 2961 (6) (*k*, *e*); 2992 (3) (*k*, *e*); 3339 (6*vb*) (*k*, *e*).

10. *Dimethyl amine hydrochloride*, $(CH_3)_2NH_2{}^+Cl^-$ (40 percent solution in water, +0.6*N* HCl). Prepared from Eastman dimethyl amine and excess HCl; recrystallized four times from alcohol-ether. Chloride calc. 43.51 percent, found 43.46 percent.

$\Delta\nu$=412 (2) (*e*); 895 (4) (*k*, *g*, *f*, *e*); 1029 (2) (*k*, *e*); 1099 (1) (*k*, *e*); 1240 (½*b*) (*k*, *e*); 1481 (4) (*k*, *e*); 2839 (1) (*k*); 2883 (1) (*k*, *e*); 2940 (½) (*k*); 2990 (5) (*k*, *i*, *e*); 3048 (4) (*k*, *i*, *e*).

11. *Trimethyl amine*, $(CH_3)_3N$, 33 percent in water. [Eastman; solution used without further purification.]

$\Delta\nu$=262 (1*b*) (*k*?, *e*); 424 (3) (*k*, ±*e*); 820 (4*b*) (*k*, *e*); 1030 (3) (*k*, *e*); 1122 (½*vb*) (*k*, *e*); 1208 (3*b*) (*k*, *e*); 1264 (½*vb*) (*k*, *e*); 1445 (5) (*k*, *e*); 1478 (5) (*k*, *e*); 2797 (6) (*k*, *i*); 2854 (6) (*k*, *e*); 2910 (1) (*k*); 2955 (4*b*) (*k*, *i*, *e*); 2980 (4*b*) (*k*, *i*).

12. *Trimethyl amine hydrochloride*, $(CH_3)_3NH^+Cl^-$ (33 percent in water, +0.6*N* (HCl). Prepared from Eastman trimethyl amine and HCl; recrystallized from alcohol-ether three times. Chloride calc. 37.13 percent, found 36.75 percent.

$\Delta\nu$=406 (1) (*e*); 468 (½) (*k*, *e*); 821 (5) (*k*, *i*, *g*, *f*, *e*); 987 (4) (*k*, *i*, *e*); 1067 (1) (*k*, *e*); 1248 (1) (*k*, *e*); 1464 (5) (*k*, *e*); 1669 (0) (*e*) (water ?); 2822 (3) (*k*); 2894 (3) (*k*, *e*); 2969 (6*vb*) (*k*, *i*, *e*); 3030 (5*b*) (*k*, *i*, *e*).

13. *Tetramethyl ammonium chloride*, $(CH_3)_4N^+Cl^-$. (45 percent aqueous solution +0.2*N* HCl.) Eastman product, three times recrystallized from alcohol-ether. Chloride calc. 32.37 percent, found 31.81 percent. As the substance is

[32] See, for instance, J. Wyman, Jr., Chem. Rev. **19**, 213 (1936); E. J. Cohn, Chem. Rev. **19**, 241 (1936).

very hygroscopic, discrepancy between observed and calculated values is probably due mostly to water.

$\Delta\nu = 372$ (2) $(\pm e)$; 455 (2) $(k, i, \pm e)$; 752 (6) $(k, i, f, \pm e)$; 955 (6) (k, i, e); 1047 (1) (k, i, e); 1173 (3) (k, i, e); 1289 (3) (k, e); 1418 (1) (k); 1455 (5) (k, i, e); 2374 ($\frac{1}{2}$) (k); 2440 (1) (k); 2598 (1) (k); 2828 (4) (k, e); 2930 (5) (k, i, e); 2967 (3) (k); 2991 (3) (k, i, e); 3037 (8) (k, i, e).

14. *Trimethyl amineoxide hydrochloride,* $(CH_3)_3N^+(OH)\,Cl^-$ (25 percent aqueous solution, $+0.2N$ HCl). Prepared from trimethyl amine and hydrogen peroxide, with subsequent addition of HCl. Four times recryst. from ethyl or methyl alcohol and ether. M.pt. 216–217° (decomp.).

$\Delta\nu = 382$ (3) (e); 500 $(2vb)$ (k, e); 754 (7) (k, f, e); 947 (7) (k, e); 1132 (2) (k, i, e); 1263 $(2b)$ (k, e); 1412 (2) (k, e); 1449 (7) (k, e); 1658 $(1vb)$ (e) (water); 2104 $(1vb)$ (k); 2186 $(1vb)$ (k); 2426 (0) (k); 2597 (2) (k); 2674 ($\frac{1}{2}$) (k); 2811 (3) (k); 2886 (3) (k); 2974 $(10vb)$ (k, i, e); 3043 $(10vb)$ (k, i, e).

15. *Sodium glycinate,* $H_2N\cdot CH_2COO^-\cdot Na^+$ [from Hoffman-LaRoche C.P. glycine twice recrystallized, +0.97 equivalent of C.P. NaOH] in water, solution containing 27 percent of glycine.

$\Delta\nu = 518$ (3) (k, e); 904 (5) (k, e); 1113 (2) (k, e); 1354 (2) (k, e); 1409 (4) (k, e); 1444 (1) (k, e); 1602 (0) (e) (water ?); 2953 (2) (k, e); 3332 (2) (k).

16. *Sodium dl-alaninate,* $H_2N\cdot CH(CH_3)\cdot COO^-Na^+$, [from Eastman dl-alanine, three times recrystallized, and 0.98 equivalent C.P. NaOH]. Aqueous solution containing 33 percent of dl-alanine.

$\Delta\nu = 543$ $(3b)$ (f, e); 853 (4) (k, f, e); 926 $(2vb)$ (k, e); 1034 ($\frac{1}{2}$) (e); 1079 (2) (e); 1162 (0) (e); 1305 ($\frac{1}{2}$) (e); 1362 (2) (k, e); 1414 (4) (k, e); 1463 (3) (k, e); 2893 (2) (k); 2946 (4) (k); 2988 (2) (k); 3313 (3) (k).

Both Na glycinate and Na alaninate show indications of a frequency near $K-3380$, obscured by heavy continuous background.

17. *Glycine,* $^+H_3N\cdot CH_2\cdot COO^-$ [23 percent solution in water]. (See reference 8.) A new study of the spectrum of this substance revealed the Raman shift 1448 cm^{-1} (1), excited by both the K and E mercury lines. The finding of this line confirms the observations of Wright and Lee, Nature, **136**, 300 (1935).

The presence of the doubtful line at 1491 in glycine, which we had previously reported, could not be confirmed.

TABLE V. *Polarization of lines in the Raman spectra studied.*

"*P*" indicates that a given line in question is strongly polarized (ρ definitely less than 6/7). "*D*" indicates that the line is nearly depolarized ($\rho = 6/7$ or not much less.)

1. *Methyl amine hydrochloride:* 995(*P*), 1466(*D*), 1625 ±50(*D*), 2975(*P*), 3032(*D*).

2. *Dimethyl amine hydrochloride:* 412(*P*), 895(*P*), 1030 (*D*), 1106(*D*), 1249(*P* ?), 1482(*D*), 2978(*P*), 3040(*D*).

3. *Trimethyl amine hydrochloride:* 406(*D*), 468(*P*), 821(*P*), 987(*D*), 1067(?), 1248(*D*), 1464(*D*), 2894(*P*), 2969(*P*), 3030(*D*).

4. *Tetramethyl ammonium chloride:* 372(*D*), 455(*D*), 752(*P*), 955(*D*), 1455(*D*), 2930(*P*), 2967(*P*), 2991(*P*), 3037(*D*).

The line at 752 cm^{-1} in tetramethyl ammonium chloride is very highly polarized (ρ approaching zero). The lines near 2980 cm^{-1} in all four compounds also are very strongly polarized.

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An Attempted Theory of Photosynthesis

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An attempt is made to explain quantitatively many observations described in the literature on the photosynthetic production of oxygen in its dependence on light intensity, time of irradiation, etc. Four photochemical steps and two dark reactions are assumed, in which among others, a peracid, formic acid and a peraldehyde occur. These are the same intermediate compounds as in auto-oxydation processes, so that the similarity between these two inverse processes is striking. Light saturation is explained by back chain reactions initiated by photolytical decomposition of the per-compounds. The agreement between observations and calculations is good. The picture gained for the photosynthesis of CO_2 can be applied in the same way for that of plant acids but the plant acids can also be photooxidized in a reaction sensitized by chlorophyll.

ABOUT a year ago one of the authors[1] published an attempt to bring the theory of photosynthesis of Willstätter and Stoll[2] into agreement with the results of modern atomic physics, especially in the field of fluorescence and spectroscopy. It was shown that this was possible in principle. One preparatory photochemical reaction, followed by the four main photochemical reactions of photosynthesis, was assumed.

Since the publication of this paper, however, it has been shown by several authors that the application of these equations presents difficul-

[1] J. Franck. Chem. Rev. **17**, 443 (1935).
[2] R. Willstätter, Naturwiss. **21**, 252 (1933); A. Stoll, ibid 20, 955 (1932); R. Willstätter and A. Stoll, *Chlorophyllbuch* (Bayr. Akad).

ties. Gaffron[3] has proved in particular that there is no necessity for the assumption of a preparatory reaction, namely the dehydrogenation of chlorophyll under the influence of oxygen and light, before photosynthesis can start. He could explain the necessity for the presence of oxygen in a much more plausible way. This point of view was therefore accepted in a paper on the fluorescence of chlorophyll by Franck and R. W. Wood.[4]

The main criticism which Gaffron and Wohl[5] level against the four proposed photochemical reactions is that the absorption of four quanta of red light supplies an energy which is ~ 20 kilocalories smaller than the heat of reaction necessary to form one molecule of formaldehyde and two of hydrogen peroxide from one of carbon dioxide and three of water. But even if one accepts these figures, they do not prove the impossibility of the original assumptions. According to the present authors,[6] one can gain sufficient energy from thermal vibrations to compensate the difference in the case of photochemical processes in polyatomic molecules, provided they show fluorescence, as is the case here. Nevertheless, it remains doubtful whether the intermediate products would be stable enough to avoid considerable back reaction, particularly for weak radiation.

Therefore, it seemed worthwhile to change the assumptions. One might question whether one should try to write specific photochemical reactions in view of our present relatively small knowledge of photosynthesis, but firstly such discussions lead to new experiments, and secondly it seems important to see whether it is possible to account for this biological problem without deviating from the usual laws of physics and chemistry.

In photosynthesis, most of the recent investigators[7] have concluded this to be impossible. They agree with Arnold, that the experiments in plants make the assumption of a photosynthetic unit necessary, in which a large number of molecules cooperate in a way not encountered in vitro. The present authors intend to show here that the assumption of such units is unnecessary and that a picture for photosynthesis can be given, into which all experiments hitherto published fit and which makes use only of the experience gained in other photochemical reactions. To do this, we shall discuss first the experiments which seem to make the "photosynthetic unit" necessary.

The name unit is given to a group of about 1000 chlorophyll molecules connected with one carbon dioxide molecule. The chlorophyll molecules of the unit are supposed to absorb light practically independently of each other, but the energy so absorbed by the whole unit is supposed to be available for the reduction of the one carbon dioxide molecule connected with it. The hypothesis was introduced to explain three groups of experiments.

Firstly, no induction period for the production of oxygen is observed for small light intensities.[8] If at the start of the illumination every individual chlorophyll molecule were connected with one carbon dioxide molecule and if four quanta would be necessary before the liberation of oxygen, the length of the induction period would be equal to the average time it takes for a chlorophyll molecule to absorb four quanta under the conditions of the experiment. This time is so long that the induction period would have been found. If on the other hand, it is only necessary for the whole unit of 1000 chlorophyll molecules to absorb four quanta, this time becomes 1000 times shorter and would be difficult to detect.

Secondly the unit explains the fact that the so-called light saturation occurs, in the presence of much CO_2, with a light intensity[9] much smaller than expected. The saturation has hitherto been explained by the occurrence of a dark reaction (Blackman reaction) in addition to the photochemical reactions in the course of photosynthesis. With intensity sufficiently high, the dark reaction would become the slowest

[3] H. Gaffron, Naturwiss. **23**, 528 (1935).
[4] J. Franck and R. W. Wood, J. Chem. Phys. **4**, 551 (1936).
[5] H. Gaffron und K. Wohl, Naturwiss. **24**, 81 (1936).
[6] J. Franck and K. F. Herzfeld, J. Phys. Chem. **41**, 97 (1927).
[7] R. Emerson and W. Arnold, J. Gen. Physiol. **16**, 191 (1932); **15**, 391 (1931); W. Arnold and H. Kohn, ibid., **18**, 109 (1934); H. Gaffron and K. Wohl, reference 5; H. J. Kohn, Nature **137**, 706 (1936); J. Weiss, Nature **137**, 997 (1936) and **138**, 80 (1936).
[8] O. Warburg, *Uber die katalyt. Wirkungen der leb. Substanz.* (Berlin, 1928).
[9] R. Emerson and W. Arnold, reference 7. More literature, see in Emerson's review, "Ergebnisse der Enzymforschung" **5**, 305 (1936).

reaction in the sequence and therefore limit the whole sequence to its own speed. The intensity at which half the saturation yield is produced would correspond to the condition that the dark reaction and the light reaction have the same speed. As the velocity of the dark reaction is known (see next paragraph) to be about 50 sec.$^{-1}$, the velocity constant of the light reaction can be calculated. It turns out so large that it again necessitates the absorption of four quanta by a unit of 1000 chlorophyll molecules for the reduction of one carbon dioxide molecule.

The third argument for the unit is independent of the assumption that four quanta have to be absorbed by any particular chlorophyll molecule to reduce one CO_2 molecule. It is based on Emerson and Arnold's[7] investigations of photosynthesis with light flashes of very short duration. The dark pauses between flashes, if long enough, allow the completion of the dark reaction. By changing these intervals, Emerson and Arnold measured the duration of the dark reaction. Changing the intensity of the light flashes, they observed a saturation for the individual flashes. The total energy absorbed per second, is, under these conditions, much smaller than the one necessary to produce saturation for continuous illumination. Arnold explains this by the assumption that all the carbon dioxide which is, at the beginning of the flash, combined with chlorophyll, is reduced by one flash and the subsequent dark reaction. The comparison between the amount of oxygen developed per flash and the amount of chlorophyll gives again about 1000 times as many chlorophyll molecules as carbon dioxide.

The agreement in the size of the unit, arrived at in the three ways (the numbers vary from 500 to 2600) has convinced most authors of the necessity of the hypothesis. The main objections are the following: Chlorophyll solutions emit fluorescent light if the chlorophyll is in true solution. Polymerization of the chlorophyll into colloidal particles made up entirely of chlorophyll destroys the fluorescence. In the plant, fluorescence occurs just as in true solutions, therefore the chlorophyll in the plant must be in molecular dispersion. We assume, however, that it is adsorbed on the surface of colloidal particles of a different material (chloroplasts). This is in agreement with the usual opinion that the chlorophyll in the plant has a colloidal distribution. The observations on fluorescence show that the individual chlorophyll molecules are separated.

In all organic (true) solutions of chlorophyll, the yield of the fluorescence is rather small.[10] This must be interpreted by the high probability of a chemical reaction of the excited chlorophyll molecule, either a dissociation of the molecule itself or some reaction with the organic solvent. Therefore, if 1000 chlorophyll molecules are coupled closely in a unit and one is excited, the major part of the absorbed energy would not be used for the reduction of CO_2, but for reactions between the chlorophyll molecules themselves. It might be added that under suitable illumination organic solutions of chlorophyll containing oxygen show the same type of change with time in the intensity of fluorescence as was found by Kautsky for leaves. Only the time scale is different.[11] This also indicates the same kind of state, i.e., molecular dispersion.

Therefore, we prefer to explain the experiments in a different way. We will assume that the saturation is due to back reactions induced by light and proceeding in chains.

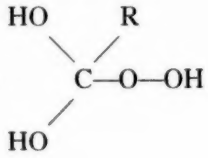
Warburg's experiments show that four quanta of red light reduce carbonic acid to the state of reduction of an aldehyde and that probably two peroxide molecules are formed, which, under the action of an enzyme, split off oxygen. The energy relations mentioned above make it improbable that H_2O_2 is the peroxide. The same is true of formic peracid[12] and formic peraldehyde, since it is known that at least the former will react with water to give formic acid and hydrogen peroxide with a negligible heat of reaction. Therefore formic peracid needs about the same energy as hydrogen peroxide.

If a peroxide is formed which needs 5–10 kcal. less than hydrogen peroxide, energy considerations present no difficulties.

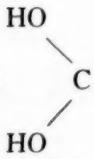
The lack of an induction period at low light intensities shows from our point of view that the peroxide is formed in the plant upon the absorption of the first quantum. Therefore, the energy

[10] J. A. Prins, Nature **134**, 457 (1934).
[11] J. Franck and H. Levi, Zeits. f. physik. Chemie **B27**, 409 (1935).
[12] See for instance, K. Wohl, Zeits. f. physik. Chemie **B31**, 152 (1935).

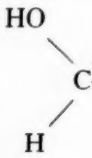
to transform carbonic acid into this peroxide cannot be larger than ~43 kcal. These considerations lead us to the following picture. We assume that in the plant the chlorophyll carbonic acid complex is attached to an organic molecule ROH present in abundance, in which the strength of the OH bond to R has the usual value of ~70 kcal. The ROH may for instance be a protein which forms the main body of the chloroplasts, on the surface of which the chlorophyll is adsorbed. The chlorophyll molecules will then be able to move along the surface as a two-dimensional gas (Vollmer). Using the data for the formation of performic acid from carbonic acid and the usual values for the C—H bonds and C—R bonds, one gets the energy necessary for



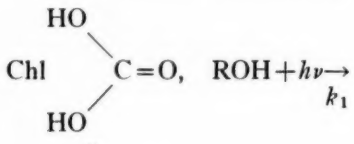
the formation of the peracid



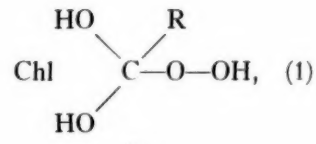
from C=O and ROH. This turns out to be a little smaller than the energy available through the first absorption act.[13] In close analogy to the first photochemical reaction, the third one is then the transformation of formic acid into the



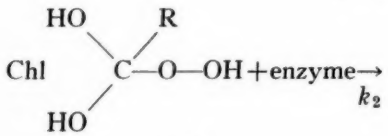
peraldehyde C—O—OH. Reactions one and three are followed by dark reactions in which the peracid or the peraldehyde is reduced under the influence of enzymes to the acid and the aldehyde. Reactions two and four transform the acid and the aldehyde into formic acid and formaldehyde and restore the catalyst ROH. So far as our knowledge of the heats of reactions which occur in these equations goes, no difficulties are encountered. At least in the first two photochemical steps, there are even available small amounts of excess energy, so that some activation energy to prevent back reaction might be present. In the following equations, concentrations x, names and constants of reaction velocities k have been written under the corresponding chemical formulas. The symbol Chl is an abbreviation for chlorophyll.



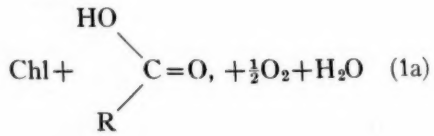
carbonic acid (x_1)



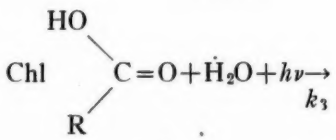
peracid (x_2) (1)



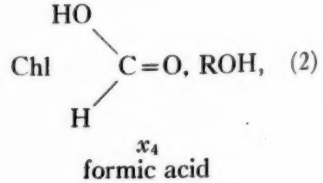
peracid (x_2)



R acid (x_3) (1a)

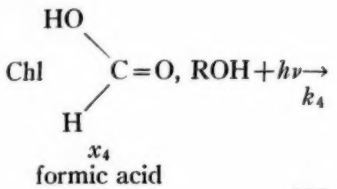


R acid (x_3)

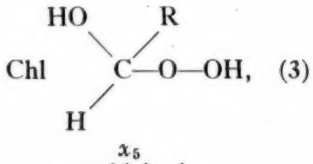


formic acid (x_4) (2)

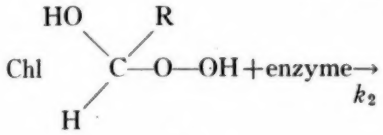
[13] We take $h\nu = 6700\text{A} \sim 43$ kcal. as the energy available for one absorption act, because $\lambda 6700\text{A}$ is the long wavelength limit of strong absorption in the chlorophyll. Ranging from 6700A toward greater wave-lengths the absorption band has a weak tail caused by the presence in the thermal distribution of a small proportion of molecules with vibration energies up to a few tenths of a volt. Absorption of these greater wave-lengths leads to the same excited state because of the contribution from thermal energy. Consequently this extra amount of thermal energy is used in addition to light energy when photosynthesis is performed with light $\lambda > 6700\text{A}$, but the absorption is this spectral region will not become appreciable unless very thick layers of chlorophyll are used.



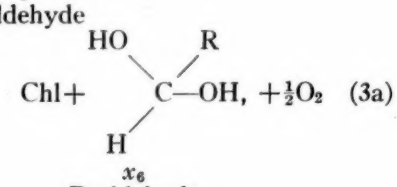
formic acid



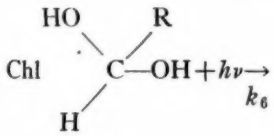
peraldehyde



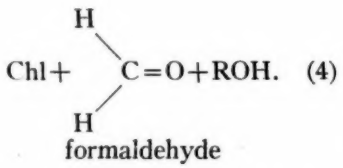
x_5
peraldehyde



R aldehyde



R aldehyde



formaldehyde

One could change Eq. (4) so that it would give glycolaldehyde instead of formaldehyde as end product, but a discussion of this question does not seem justified at the present stage. We do not suppose that the preceding equations represent any final solution, but they explain so many facts that they are at least a good working hypothesis;[14] the assumption that the peroxides[15] mentioned above are intermediate products of photosynthesis makes the photoreduction of carbonic acid and formic acid entirely analogous to the reverse processes of autoxydation of aldehydes to formic acid and carbonic acid, as observed in vitro. The photochemical equations thus gained for photosynthesis can be applied in the same way to the photosynthesis of plant acids formed as intermediate states of respiration. The only difference between these higher acids on the one hand, and carbonic acid on the other, is that the latter will only undergo photosynthesis, while the former will also be photoxidized under suitable conditions. This photooxidation provides for the explanation of the Kautsky[16] curves of fluorescence and the induction period,[8] both observed only with strong illumination in the presence of oxygen.

It is particularly important that the binding energy of —OH to —O— in both the peroxides used above is so weak (<40 kcal. according to calculations from the heat of formation), that the radical —OH will be split off whenever the complex Chl peracid or Chl peraldehyde absorbs a quantum of light. This fact gives an explanation for the shape and the constants of the saturation curves, both for continuous and flashing light. The probability of such an absorption is negligible with weak illumination because the average time between two absorption acts of a chlorophyll molecule is much greater than the time within which the enzyme reduces the permolecule. But if the light intensity is increased, this probability becomes greater. It is about 1/10 for an intensity that gives almost saturation in normal leaves. (This value is calculated from the velocity of the Blackman reaction, the number of light quanta impinging per second, and the number of chlorophyll molecules in the leaf.) The photodecomposition of the permolecule into two radicals will then start chain reactions in the usual way. In our case, these *chain reactions are back reactions* of the peracid to carbonic acid and ROH, and of

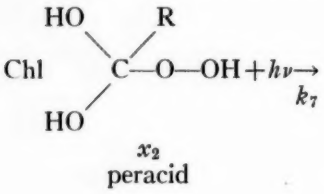
[14] Following the ideas of Weiss, reference 7, one might try to replace the catalyst ROH used in the preceding equations by Ferri ions. But not enough iron is present in the plant to provide each chlorophyll molecule with an Fe ion. Moreover, Warburg[8] has shown that while the Blackman reaction (and photosynthesis at high light intensities) is influenced by cyanide in a way typical for a Fe catalysis, photosynthesis at low intensities is not affected. He concludes therefore that Fe catalysis does not play any role in the purely photochemical part of photosynthesis.

[15] Compare R. Willstätter and A. Stoll, reference 2.

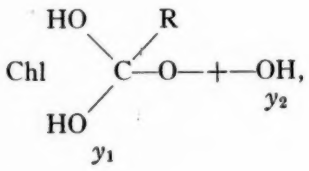
[16] H. Kautski and co-workers, Naturwiss **19**, 964 (1931); **19**, 1043 (1931), and **24**, 317 (1936). Ber. d. Dtsch. Chem. Ges. **65**, 1762 (1932); **66**, 1588 (1933) and **68**, 152 (1935). Biochem. Zeits. **274**, 423 (1934); **278**, 373 (1935) and **284**, 412 (1936).

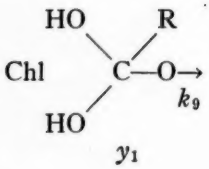
the peraldehyde to formic acid and ROH. The following equations describe tentatively these chains.

There are two photochemical reactions (5) and (6) both splitting off the weakly bound OH, one for the peracid, one for the peraldehyde. In each case there are two possibilities for chains, one with —R(Eqs. (a) and (b)), one with —OH (Eqs. (d) and (e)) and there are two reactions terminating the chain ((c) and (f)). We write again concentrations (y for the radicals) and velocity constants below the chemical equations

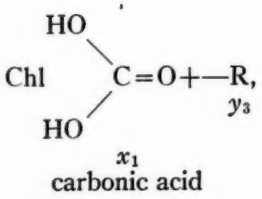


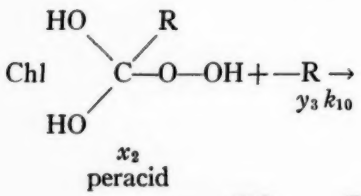
(5)





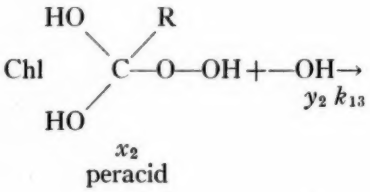
(5a)

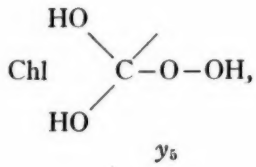




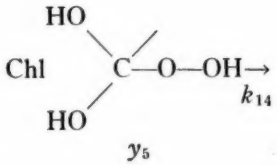
(5b)

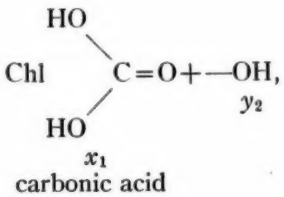
Disappearance of —R $k_{23}y_3$, (5c)





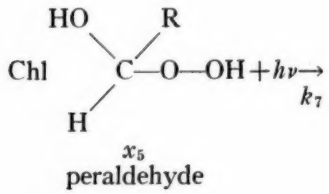
(5d)



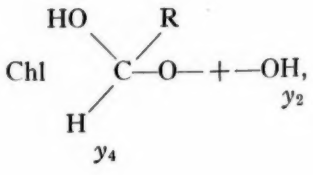


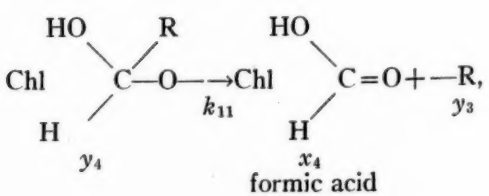
(5e)

Disappearance of —OH $k_{22}y_2$, (5f)

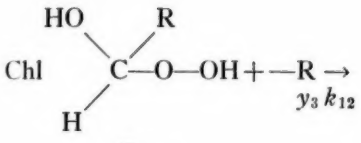


(6)

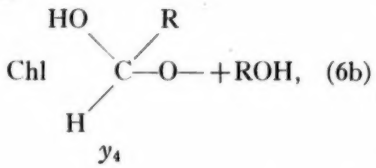




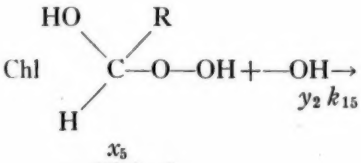
(6a)



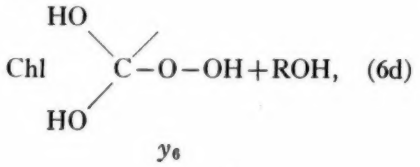
peraldehyde

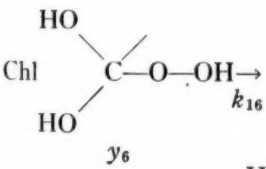


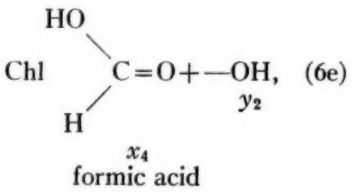
(6c) = (5c)



peraldehyde







formic acid

(6f) = (5f)

Differential Equations for the Reactions

We write the equations for the different compounds which occur in the course of photosynthesis (concentrations x_2 to x_6) and of the radicals occurring in the chains (concentrations y_1 to y_6). It should be remembered that x_2 and x_5 are the concentrations of the peracid and peraldehyde respectively, and that k_1, k_3, k_4, k_6, k_7 are proportional to the light intensity I and as the absorption occurs in the chlorophyll, all equal, namely equal to the rate of light absorption in chlorophyll.

$$dx_2/dt = k_1x_1 - k_2x_2 - k_7x_2 - k_{10}x_2y_3 - k_{13}x_2y_2, \quad (7)$$

$$dx_3/dt = k_2x_2 - k_3x_3, \quad (8)$$

$$dx_4/dt = k_3x_3 - k_4x_4 + k_{11}y_4 + k_{16}y_6, \quad (9)$$

$$dx_5/dt = k_4x_4 - k_2x_5 - k_7x_5 - k_{12}y_3x_5 - k_{15}y_2x_5, \quad (10)$$

$$dx_6/dt = k_2x_5 - k_6x_6, \quad (11)$$

$$dy_1/dt = k_7x_2 - k_9y_1 + k_{10}x_2y_3, \quad (12)$$

$$dy_2/dt = k_7(x_2+x_5) - k_{13}y_2x_2 + k_{14}y_5 - k_{15}y_2x_5 + k_{16}y_6 - k_{22}y_2, \quad (13)$$

$$dy_3/dt = k_9y_1 - k_{10}x_2y_3 + k_{11}y_4 - k_{12}y_3x_5 - k_{23}y_3, \quad (14)$$

$$dy_4/dt = k_7x_5 - k_{11}y_4 + k_{12}x_5y_3, \quad (15)$$

$$dy_5/dt = k_{13}x_2y_2 - k_{14}y_5, \quad (16)$$

$$dy_6/dt = k_{15}y_2x_5 - k_{16}y_6. \quad (17)$$

In these equations we have assumed the chains to be terminated by the first order disappearance of the radicals OH and R, $-k_{22}y_2$ and $-k_{23}y_3$. It will be shown afterwards that a first order reaction is necessary to give saturation. That y_2 and y_3 alone have been chosen is due to the fact that the other radicals y_1, y_5, y_4, y_6 are very unstable so that the amount of R— and —OH is much greater than that of the large radicals and so the overwhelming number of chains is terminated by reactions taking R and OH out of the chain.

Adding, on the one hand (12), (14) and (15), on the other (13), (16) and (17), finally (8), (9), (10), (15) and (17) gives

$$(d/dt)(y_1+y_3+y_4) = k_7(x_2+x_5) - k_{23}y_3, \quad (18)$$

$$(d/dt)(y_2+y_5+y_6) = k_7(x_2+x_5) - k_{22}y_2, \quad (19)$$

$$(d/dt)(x_3+x_4+x_5+y_4+y_6) = k_2(x_2-x_5). \quad (20)$$

Furthermore, if N is the total number of chlorophyll molecules taking part in photosynthesis, we have

$$N = x_1+x_2+x_3+x_4+x_5+x_6 \quad (21)$$

the number of radicals being too small to count.

The Chain Equations

With stationary illumination, all the left sides of Eqs. (7) to (20) are zero. Therefore, (18) and

(19) determine the concentration of the R— and —OH radicals. Eqs. (18) and (19) say, of course, that the stationary state for the concentrations of the radicals is reached if for every percompound dissociated by light one R— and one —OH are destroyed by the chain-ending reactions. If we put these results into Eqs. (12), (15), (16), (17) equated to zero, we find the following equations for the radicals

$$y_2=(k_7/k_{22})(x_2+x_5), \tag{22}$$

$$y_3=(k_7/k_{23})(x_2+x_5), \tag{23}$$

$$y_5=\frac{k_{13}}{k_{14}}x_2y_2=\frac{k_{13}}{k_{14}}\frac{k_7}{k_{22}}x_2(x_2+x_5), \tag{24}$$

$$y_1=\frac{1}{k_9}(k_7x_2+k_{10}x_2y_3)$$

$$=\frac{k_7}{k_9}x_2\left\{1+\frac{k_{10}}{k_{23}}(x_2+x_5)\right\}, \tag{25}$$

$$y_4=\frac{1}{k_{11}}(k_7x_5+k_{12}x_5y_3)$$

$$=\frac{k_7}{k_{11}}x_5\left\{1+\frac{k_{12}}{k_{23}}(x_2+x_5)\right\}, \tag{26}$$

$$y_6=\frac{k_{15}}{k_{16}}y_2x_5=\frac{k_7}{k_{22}}\frac{k_{15}}{k_{16}}x_5(x_2+x_5). \tag{27}$$

We abbreviate

$$Z=k_{10}/k_{23}+k_{13}/k_{22}, \tag{28}$$

$$Z'=k_{15}/k_{22}+k_{12}/k_{23}, \tag{28'}$$

We now substitute the values found for the radical concentrations back into (7) to (11)

$$dx_2/dt=k_1x_1-x_2\{k_2+k_7+k_7Z(x_2+x_5)\}, \tag{7'}$$

$$dx_3/dt=k_2x_2-k_3x_3, \tag{8'}$$

$$dx_4/dt=k_3x_3-k_4x_4+k_7x_5\{1+Z'(x_2+x_5)\}, \tag{9'}$$

$$dx_5/dt=k_4x_4-x_5\{k_2+k_7+k_7Z'(x_2+x_5)\}, \tag{10'}$$

$$dx_6/dt=k_2x_5-k_6x_6. \tag{11'}$$

We name now two assumptions, which are in no way necessary to our physicochemical considerations, but lighten the mathematical task so far as the flash illumination is concerned.

Firstly, we assume

$$Z=Z', \tag{28''}$$

which means that the speed of reaction of the peracid with the radicals R and OH is the same as that of the peraldehyde with the same radicals, which seems plausible.

Secondly, we assume that the duration of the chains is short even compared with the duration of a flash (10^{-5} sec.) so that the concentrations of the other molecules have not changed appreciably during the time between the starting and the ending of one chain. In this case, formulas (22) to (27) for the concentrations of the radicals, which have been calculated for constant concentration, can still be used with concentrations of the molecules x_2, x_5 varying with time, the variation during the life of one chain being assumed small.

Under these assumptions, one can talk uniformly about both continuous and flash illumination.

As the number of chains starting per second is given by k_7x_2 and k_7x_5, and the total number of chain reactions $k_7Z(x_2+x_5)x_2$ and $k_7Z(x_2+x_5)x_5$ (see 7', 9', 10'), it follows that the chain length is $Z(x_2+x_5)$.

Continuous Illumination

Then, in the steady state, the left side of Eqs. (7') to (11') and (20) are zero. Taking into account the equality of all the light reaction constants, one finds

$$x_2=x_5, \quad x_3=x_6=k_2x_2/k_1, \quad x_4=x_1, \tag{29}$$

$$k_1x_1=x_2\{k_2+k_1+2Zk_1x_2\}, \tag{30}$$

$$N=2x_1+2x_2+2(k_2x_2/k_1), \tag{21'}$$

or $$(N/4)k_1=x_2\{k_2+k_1+Zk_1x_2\}. \tag{31}$$

If we call the number of oxygen molecules developed per second V, we have

$$V=\tfrac{1}{2}k_2(x_2+x_5)=k_2x_2 \tag{32}$$

or $$\frac{N}{4}k_1=V+Z\frac{k_1}{k_2^2}V^2 \tag{31'}$$

k_1 can always be neglected[17] next to either k_2 or

[17] If the intensity is weak, $k_1<k_2$. If the light is strong $k_1<k_2Z(x_2+x_5)$.

Zk_1x_2 and has been left out. The equation shows clearly the behavior of the system. If the light intensity is small, the second member on the right side is small compared with the first, i.e., the action of the enzyme can catch up with the production of the percompounds and nothing is lost by back photoreaction. The yield is $\frac{1}{4}$:

$$V=(N/4)k_1. \qquad (31'')$$

From (30) follows $k_2x_2 \sim k_1x_1$; (29) gives then

$$x_1=x_4=x_3=x_6.$$

The chlorophyll is occupied one-fourth each by $CO_2(x_1)$, R acid (x_3), formic acid (x_4) and R aldehyde (x_6), the percompounds being decomposed too rapidly to count. With increasing intensity, more and more of the percompounds are consumed by the chains before the enzyme has time to act, until saturation is reached, given by

$$V^2_{max}=(N/4)(k_2^2/Z),$$
$$V_{max}=Nk_2(1/4NZ)^{\frac{1}{2}}. \qquad (33)$$

The quantity $(4/NZ)^{\frac{1}{2}}$ is the factor by which the yield is smaller than it would be if the Blackman reaction were alone (i.e., in the absence of chain back reactions) responsible for saturation ($V=(N/4)k_2$); it should therefore be 1/500 to 1/2500, or $NZ \sim 10^6$ (10^6 corresponds to the first, $25 \cdot 10^6$ to the second number) which is not unreasonable for the chain length for unit concentration of the percompound (the chain length in photosynthesis at saturation is only $\sim 10^3$, as $x_2 \sim N \cdot 10^{-3}$). At saturation, CO_2 and formic acid occupy each almost half of the chlorophyll, the R acid and R aldehyde small fractions, the percompounds still less (since k_2 still $>k_1$).

The equation for the dependency of V on the light intensity I can be written, from (31′) and (33)

$$KI=V/(1-V^2/V^2_{max}), \qquad (34)$$

with $K=(N/4)(k_1/I)$. This is plotted in Figs. 1 and 2 and shows good agreement with the measurements, which are discussed by Smith[18] and other observers, although the form is different from the one suggested by Smith. It explains also the dependency of photosynthesis on chlorophyll, as only the amount of light absorbed counts and N enters in the same way as I. Therefore, photosynthesis has the same dependence on the amount of chlorophyll as on light intensity. If the amount of CO_2 adsorbed is proportional to the external CO_2 pressure, the same relation should hold for the dependency on CO_2 pressure. In fact, Smith represents the dependency of photosynthesis on CO_2 by the same curve as the dependency on light intensity.

[18] E. Smith, Nat. Acad. of Sciences America **22**, 504 (1936).

Flash Saturation

We consider the stationary state, when the flashing has gone on for some time and the effects of subsequent flashes are all equal. We call the beginning of a flash time 0, its end time τ, the duration of the dark interval T. In the stationary state, everything must be the same at $t=T+\tau$, when the next flash starts, as it was at $t=0$.

During the dark period, we have the following equations

$$dx_2/dt=-k_2x_2, \qquad (7'')$$
$$dx_3/dt=k_2x_2, \qquad (8'')$$
$$dx_4/dt=0, \qquad (9'')$$
$$dx_5/dt=-k_2x_5, \qquad (10'')$$
$$dx_6/dt=k_2x_5. \qquad (11'')$$

That gives

$$\left.\begin{aligned} x_2&={}_\tau x_2(1-e^{-k_2t}) \\ x_5&={}_\tau x_5(1-e^{-k_2t}) \end{aligned}\right\} t \text{ counted from } \tau. \qquad (35)$$

Integrate then (20) from $t=0$ to $t=\tau+T$. We have then as the left side the difference of $x_3+x_4+x_5+y_4+y_6$ at these two moments, which difference is zero. On the right, there is no light reaction, and we can therefore neglect the integration over the very short flash. We find, therefore,

$${}_\tau x_2(1-e^{-k_2T})={}_\tau x_5(1-e^{-k_2T}),$$

or ${}_\tau x_2={}_\tau x_5$, and, therefore, x_2 and x_5 are equal during the dark period.

Now on comparing (10′) with (7′), one sees that this is possible if $x_1=x_4$, because then the equations for x_2 and x_5 become identical, and if these quantities are equal at one moment, they will remain so.

Even for the largest available intensities, only a small fraction of the chlorophyll molecules absorb a quantum during one flash (according to

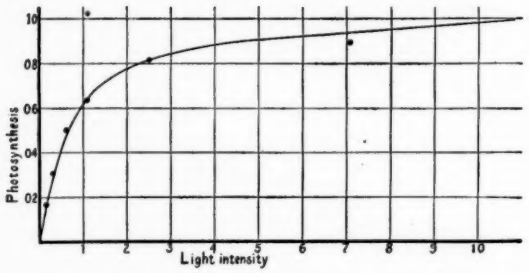


FIG. 1. Degree of saturation for continuous illumination as function of the light intensity. Abscissa: light intensity. The units are such that intensity 1 means that four times as many light quanta are absorbed as oxygen molecules are developed at saturation. The curve is calculated according to Eqs. (31′), (34). The measurements are from Warburg.[8]

Kohn's[7] data, ~0.01). Therefore, the relative change that the number of molecules of any kind which are not reacting during the dark (i.e., all except the percompounds) undergoes during one flash is small, and we can substitute the average value. We find therefore from (8′), (8″)

$$k_3\bar{x}_3\tau=\int_\tau^T k_2x_2dt={}_\tau x_2(1-e^{-k_2T}), \qquad (36)$$

which says that during the flash just as much R acid is transformed into formic acid as is supplied in the dark interval by decomposition of peracid. Similarly from (11′), (11″)

$$k_6\bar{x}_6\tau=\int k_2x_5dt={}_\tau x_2(1-e^{-k_2T}). \qquad (36')$$

We call v the amount of oxygen developed per flash (not per second), which is

$$v=\tfrac{1}{2}\int k_2(x_2+x_5)dt={}_\tau x_2(1-e^{-k_2T}). \qquad (37)$$

Neglecting during the flash k_2, we get by integrating the equation (see 7′)

$$dx_2/dt=k_1\bar{x}_1-2k_1Zx_2^2 \qquad (7''')$$

the following result

$$\frac{(k_1x_1)^{\frac{1}{2}}-(2k_1Z)^{\frac{1}{2}}x_2}{(k_1x_1)^{\frac{1}{2}}+(2k_1Z)^{\frac{1}{2}}x_2}=\frac{(k_1x_1)^{\frac{1}{2}}-(2k_1Z)^{\frac{1}{2}}{}_0x_2}{(k_1x_1)^{\frac{1}{2}}+(2k_1Z)^{\frac{1}{2}}{}_0x_2}$$

$$\times\exp.\left(-2k_1x_1\left(\frac{2Z}{x_1}\right)^{\frac{1}{2}}t\right) \qquad (38)$$

in which x_1 has been written instead of $\bar{x}_1$ but

$${}_0x_2={}_T x_2={}_\tau x_2e^{-k_2T}.$$

One has, in addition, from (21′), (36)

$$N/2=x_1+{}_\tau x_2\{1+(1/k_1\tau)(1-e^{-k_2T})\},$$

or, neglecting $k_1\tau$ compared to 1 and assuming $k_2T>k_1\tau$

$$(N/2)k_1\tau-{}_\tau x_2(1-e^{-k_2T})=k_1\tau x_1. \qquad (21'')$$

Writing now simply x instead of ${}_\tau x_2$, one gets as equation for the unknown x as function of $k_1\tau$ and T

$$\frac{[(N/2)k_1\tau-x(1-e^{-k_2T})]^{\frac{1}{2}}-(2k_1\tau Z)^{\frac{1}{2}}x}{[(N/2)k_1\tau-x(1-e^{-k_2T})]^{\frac{1}{2}}+(2k_1\tau Z)^{\frac{1}{2}}x}$$

$$=\frac{[(N/2)k_1\tau-x(1-e^{-k_2T})]^{\frac{1}{2}}-(2k_1\tau Z)^{\frac{1}{2}}xe^{-k_2T}}{[(N/2)k_1\tau-x(1-e^{-k_2T})]^{\frac{1}{2}}+(2k_1\tau Z)^{\frac{1}{2}}xe^{-k_2T}}$$

$$\times\exp.\left\{-2(2k_1\tau Z)^{\frac{1}{2}}\left[\frac{N}{2}k_1\tau-x(1-e^{-k_2T})\right]^{\frac{1}{2}}\right\}. \qquad (39)$$

This formula is too complicated to be discussed for all possible cases. We see, however, that if the light is very weak ${}_\tau x_2=k_1x_1\tau+{}_0x_2$ {from (7′)}. (No chain back reactions, all percompounds formed are still present at the end of the flash,

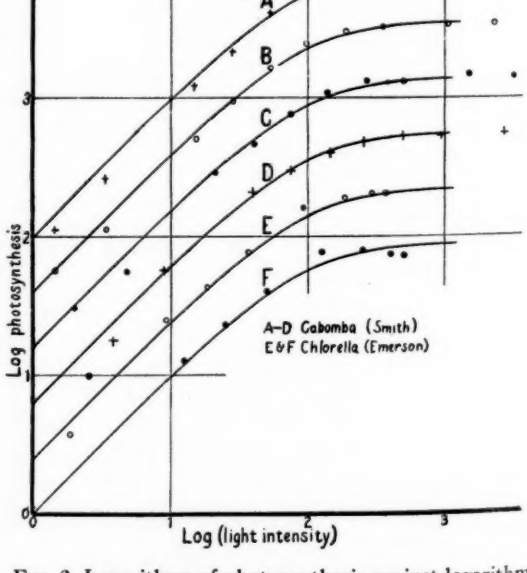


FIG. 2. Logarithms of photosynthesis against logarithms of light intensities. The curves are calculated according to Eqs. (31′), (34), but the absolute values are not given. The points mark experimental data. The measurements are taken from E. Smith.[18]

time τ.) Then

$$x_1 = N/4$$

and as with weak continuous light, the chlorophyll is equally divided between CO_2, R acid, formic acid and R aldehyde.

$$v = {}_{r}x_2(1-e^{-k_2 T}) = {}_{r}x_2 - {}_{0}x_2 = k_1 x_1 \tau = k_1 (N/4)\tau.$$

The amount of oxygen developed per flash is proportional to the light energy, with quantum yield $\frac{1}{4}$, independent of the interval between flashes.

If, on the other hand, the light intensity is high enough to give flash saturation, the exponent on the right side of (39) is very large and therefore,

$$(N/2)k_1\tau - x(1-e^{-k_2 T}) = 2k_1\tau Z x^2,$$

but the second member on the left is also small and we have

$$x^2 = N/4Z. \tag{39'}$$

That means simply that the stationary concentration of the percompounds is established during the duration of the flash, independently of whether at the beginning of a flash any remnants from the preceding flash are still present. The back reaction chains are working so fast, that these remnants are consumed, and the concentrations of the percompounds is the same as in continuous light (where it would, however, take much longer to establish the steady state, due to the smaller intensity of the light used).

During a dark interval $T < 1/k_2$ however, not all of the percompounds can be decomposed enzymatically before the chains of the next flash destroy them, and so we find

$$v_{sat} = (N/4Z)^{\frac{1}{2}}(1-e^{-k_2 T}), \tag{39}$$

giving the correct experimental dependance on T. If T is $\sim 1/2k_2$ the production of O_2 *per second* is about 80 percent of that produced at saturation by continuous illumination, at $T = 1/k_2$, about 63 percent.

The variation of v with light intensity will be discussed only for long dark intervals ($k_2 T \gg 1$), so that the equation takes the following form

$$\frac{((N/2)k_1\tau - v)^{\frac{1}{2}} - (2k_1\tau Z)^{\frac{1}{2}} v}{((N/2)k_1\tau - v)^{\frac{1}{2}} + (2k_1\tau Z)^{\frac{1}{2}} v} = \exp.\{-2(2k_1\tau Z)^{\frac{1}{2}}((N/2)k_1\tau - v)^{\frac{1}{2}}\}. \tag{40}$$

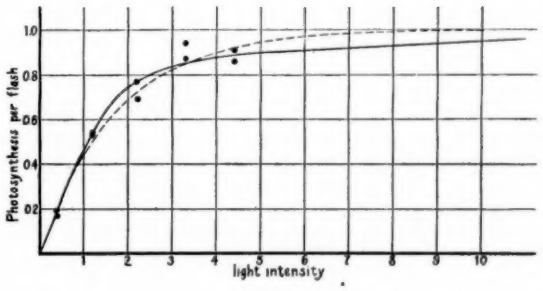


FIG. 3. Photosynthesis per flash in intermittent light. Ordinate photosynthesis as fraction of saturation value. Abscissa light intensity. The full curve is calculated from Eq. (40'). Units so that light intensity 1 means: Per flash there are twice as many quanta absorbed as molecules of oxygen are produced at saturation. The dotted curve is calculated from the Eq. (1) $-v/V_{max} = \exp. - 0.575\ I$ which has the form suggested by Kohn.[7] The points are experimental results by R. Emerson and W. Arnold.[7]

Call again $$V_{max} = (N/4Z)^{\frac{1}{2}}, \tag{41}$$

so that $$N/V_{max} = (4NZ)^{\frac{1}{2}} \tag{41'}$$

is the ratio of chlorophyll molecules present to oxygen molecules produced per flash at saturation.

Call $$v' = (N/2)k_1\tau \tag{41''}$$

half of the numbers of quanta absorbed per flash. Then

$$\frac{(1-v/v')^{\frac{1}{2}} - v/V_{max}}{(1-v/v')^{\frac{1}{2}} + v/V_{max}} = \exp.\left\{-2\frac{v'}{V_{max}}\left(1-\frac{v}{v'}\right)^{\frac{1}{2}}\right\}. \tag{40'}$$

The equation was solved numerically,[19] the result is plotted in Fig. 3. Kohn has made plausible the form

$$1 - v/V_{max} = \exp.(-kI).$$

The main reason why our curve deviates from this is the shift in the amount of carbonic and formic acid from $\frac{1}{4}$ of the chlorophyll each at low intensities to $\frac{1}{2}$ each at saturation. However,

[19] This was done by writing (40') in the form

$$\frac{1-v/v'}{v/v'} = u\frac{1+e^{-2u}}{1-e^{-2u}} \text{ with } u = \frac{v'}{V_{max}}\left(1-\frac{v}{v'}\right)^{\frac{1}{2}},$$

calculating the left side for a set of values of u and then from u and the so found

$$\frac{1-v/v'}{v/v'} = \frac{v'}{v} - 1, \text{ finding } \frac{v'}{V_{max}} \text{ and } \frac{v}{V_{max}}.$$

Kohn's curve deviates appreciably from ours only quite close to saturation, as Fig. 3 shows. The numerical values of Kohn would lead to

$$(4NZ)^{\frac{1}{2}} \sim 1000$$

(1 mm³ of oxygen $= 2.7 \cdot 10^{16}$ molecules in 3 minutes $= 3 \times 60 \times 15 = 2700$ flashes, i.e., 10^{13} molecules of oxygen per flash, $\sim 10^{16}$ molecules of chlorophyll) in fair agreement with the values for continuous illumination. But his light intensity

$$k_1\tau = 0.01, \quad \text{i.e.,} \quad v' = \tfrac{1}{2} \cdot 10^{14}, \quad v'/V_{\max} = 5$$

would lead to 90 percent saturation instead of the 99 percent he claims.

Discussion of the Assumptions

The explanation of saturation by dark back reaction is out of the question. If it were monomolecular, it would affect the yield in weak light just as much as in strong light; if bimolecular, it would give a yield proportional to the square root of light intensity instead of saturation.

Therefore, the back reaction must be contingent on light. The first question to decide is whether the final product, oxygen, is consumed or the percompounds, peracid and peraldehyde. This question can be decided from a consideration of flash saturation. Oxygen is produced by the action of enzyme on the percompound, which is so slow (50 sec.$^{-1}$) that only a negligible amount is produced during the flash itself (duration $< 10^{-4}$ sec.). Therefore, if flash saturation is to be explained by O_2 consumption, we would have to assume a persistent oxygen level. If this came from the outside (equilibrium with atmosphere) one would not get saturation, as one would have to subtract from a production of O_2 proportional to I (light intensity) a consumption proportional to I or I^2, leaving either something $\sim I$ or something falling off to zero after a maximum. If the level is determined by production and consumption of oxygen—which means assuming the escape slow compared with the production—then one would have this level independent of the distance between flashes and increasing oxygen development per flash with increase of the interval between flashes, i.e., the time available for oxygen escape, contrary to experience. Therefore, for flash illumination the back reaction must affect the percompounds only.

If in continuous illumination both percompound and oxygen would be consumed, one would not get saturation; because a mechanism giving saturation in flash illumination would make the percompounds independent of light intensity as in flash saturation, therefore the amount of oxygen produced would be independent of the intensity and an additional consumption of oxygen would make the amount escaping decrease with increasing high intensity.

Of course, this does not mean that the radicals do not react with oxygen at all. This would be contrary to the experience with the oxidation of aldehydes by oxygen. It only means that the radicals react much faster with the peroxides than with oxygen, probably because the heat of activation for a reaction between radical and oxygen is considerably higher than for a reaction between the radical and peroxide. That is quite plausible in view of the stability of the oxygen molecule and the instability of the peroxides.

Now the peracid is produced proportional to the first power of I. To get saturation for continuous light, the consumption must (at high light intensity) also be proportional to I and some powers of the concentration x_2 of the peracid, as is seen from

$$\text{production} \sim I = \text{consumption } I x_2^{s}.$$

That only first powers in I occur follows also from the experimental result of Emerson and Arnold,[7] that photosynthesis depends only on the product of light intensity and duration of the flash. During the flash everything but photoprocesses can be ignored. One divides then the kinetic equations by I. On the left, Idt appears in the denominator, and no other I should appear in the equations.

This being recognized, the back reaction (consumption of the percompound) must depend on the absorption of light by the percompound. But according to Kohn's data only a small fraction of the peroxide produced during one flash can have occasion to absorb a light quantum. Nevertheless, most of it must be consumed by the back reaction before it can be decomposed by enzyme, as the oxygen developed is only a fraction of the peroxide produced (i.e., of the

number of light quanta absorbed). Therefore the few optically excited permolecules must start long chains which consume most of the permolecules. But this consumption, as said before, must be proportional to the light intensity, i.e., to the number of chains that have been started. That is only possible if the ending of the chain occurs in a reaction containing the chain carrier in the first order, as in (5c) and (5f). Had we assumed an ending of the chain by a reunion of two radicals, the rate of production of oxygen would be proportional to the square root of the number of chains started, i.e., to the square root of the light intensity, and there would be no saturation. A first-order ending of the chains might be explained by the destruction of the radicals in a heterogeneous reaction, which is quite plausible. The power in which the concentration of the peroxide enters the equation does not affect the fact of saturation (provided it is positive), but the way in which saturation is reached. Our equations lead to a chain length proportional to the concentration of the percompound. This is responsible for the good agreement with the experimental curves. Had we taken also the ending of the chain to be proportional to the percompound, $k_{22} \sim k_{22}' x_2$, the chain length would have been constant, and the formula for continuous illumination would have been the usual one

$$KI = V/(1 - V/V_{max})$$

which does not agree so well with Smith's results.

Time of Approach to Steady State

If we start out with a plant that has been in the dark for a long time in the presence of a great excess of CO_2, we can assume that practically all the chlorophyll molecules are connected with carbonic acid.

We want to calculate the order of magnitude of the time it takes to reach the stationary state with high light intensity.

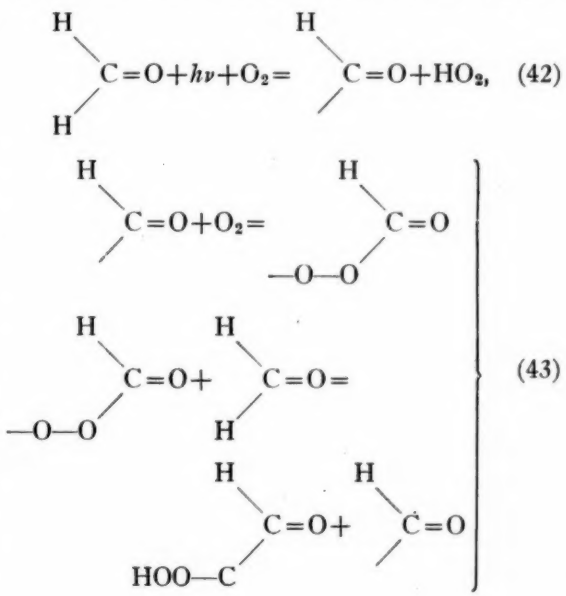
The intermediate substance which is present in the stationary state in the greatest amount is formic acid, namely in an amount equal to that of CO_2, or about half that of chlorophyll. Now the reaction that limits the production of formic acid is essentially the enzyme decomposition of the peracid, the next stage—the R-acid—being present in such a small quantity that its stationary state is reached much more quickly.

In saturation for continuous illumination, Emerson and Arnold find a production of about $2 \cdot 10^{-10}$ mole of O_2 per second for $0.5 \cdot 10^{-8}$ mole of chlorophyll, or a production of 1/25 molecule of peracid per second per molecule of chlorophyll. Therefore, the order of magnitude of the time necessary to reach the stationary state will be somewhat larger than 25 seconds, or about 1 minute. For flash saturation, the same authors get $2 \cdot 10^{-12}$ mole O_2 per flash under the same conditions, or 1/2500 molecules of peracid per molecule of chlorophyll per flash, which agrees well with Kohn. Therefore, one would need somewhat more than 2500 flashes, or about 3 minutes in Kohn's experiment.

Oxidation Processes

As was mentioned above, the intermediate products of the four photochemical steps of photosynthesis are very similar to the intermediate compounds that are generally assumed to occur in autoxidation processes in vitro, both in those induced by light and in those which occur at high temperatures.[20] Of course, the oxidation processes, being strongly exothermic, proceed by chains, which is not the case in photosynthesis.

We may use as an example the photochemical oxidation of formaldehyde by molecular oxygen:



(42)

(43)

The peraldehyde then reacts with aldehyde to give formic acid.

In plants, the intermediate products of respiration will be particularly affected by photooxidation. There are different opinions about the mechanism of the oxidation which goes on under the influence of the respiration ferment, but doubtlessly acids of the same level of oxidation as formic and carbonic acid occur as intermediate products. As higher carbohydrates are oxidized, these intermediate products are more complicated than H_2CO_3 or H_2CO_2, but we see no reason why these plant acids should be photosynthesized in a way different from that for H_2CO_3, as Warburg has concluded. His experiments can also be interpreted in a different manner and his opinion seems to us to be in contradiction with some experiments of Emerson and Arnold.

In the plant acids, the photooxidation by oxygen molecules—possible only if the acids are adsorbed to chlorophyll—can take place in all the side branches, and is therefore much more probable under the same conditions than in formic acid.

If the plant has been in the dark for some time, a considerable amount of those plant acids will have accumulated by respiration. The stationary concentration is much higher in the dark than in light, since the acids are transformed photochemically into aldehydes (reduction) and carbonic acid (photooxidation). Even in the presence of much CO_2, a part of the chlorophyll will be occupied by adsorbed plant acids after a certain time in the dark.

If we now start an illumination, every quantum absorbed by a chlorophyll with an attached CO_2, and a majority absorbed by chlorophyll with plant acids attached, will start photosynthesis, producing directly peracids or peraldehydes in the first step. Some quanta, however, will be absorbed by chlorophyll molecules which have plant acids absorbed, at a moment when an O_2 molecule is in contact with the latter. In this case, a radical will originate from this complex (42), starting a chain which uses molecular oxygen to build up a considerable number of peracid molecules (43). Because of the many side chains of the plant acids, we cannot neglect the chains with oxygen here, as we did with CO_2 and H_2CO_2. Therefore, in this stage, peracid or peraldehyde is formed, partly with a consumption of oxygen.

There exists in consequence an induction period[8] with a diminished oxygen production and diminished CO_2 consumption which lasts until the concentration of the plant acids is reduced to the value corresponding to the stationary state for illumination. Therefore for strong light this induction period should be shorter than for weak light.

On the other hand, the total underproduction of oxygen during the induction period will be much larger for strong light,[21] as the peracids will be able to form radicals by absorption of light before they are decomposed by enzyme. These radicals start chains partially compensating photosynthesis, as has been shown in (5) and (6). These chains are rapid compared with the chains involved in photooxidation. Due to the photooxidation of the plant acids, there are now more chains starting back reaction in comparison with the quantity of peracid involved in photosynthesis than would be the case without the plant acids.

The slight dependence of the yield of photosynthesis under strong illumination on the external pressure of oxygen, which Warburg found, can also be explained. Even in the stationary state with strong illumination, there will be produced a certain amount of plant acids by respiration, which will then be partly photosynthesized, partly photooxidized. The photooxidation constitutes a small steady drain on the oxygen developed. The division between photosynthesis and photooxidation is shifted toward photooxidation with an increasing amount of O_2 present, until the limiting state observed by Warburg is reached.

If one strongly illuminates leaves in the presence of oxygen, they emit fluorescent light with an intensity which changes with time of irradiation. The intensity increases rapidly in the first second of the illumination, reaches a maximum and falls off slowly to a stationary

[20] See, for instance, the theory of H. L. T. Baeckström, Zeits. f. physik. Chemie **B25**, 99 (1934), and the discussion in the Bunsengesellschaft in July, 1936; Zeits. f. Elektrochemie **42**, 439–498 (1936).

[21] The effect has in fact not yet been found for weak light.

value. This behavior and the existence of the induction period can be explained in the same way. The explanation for the form of the dependency of the fluorescent light on time has been given by Franck and Wood. There are no reasons to change the general conclusions, but it is now possible to come to a more definite picture in respect to the chemical substances involved. After a dark pause part of the chlorophyll in the leaf has adsorbed plant acids which will use the absorbed light for photosynthesis and for photooxidation. Therefore the fluorescence is weak in the first moment of illumination. The chain reaction of photooxidation produces radicals in the side branches of the plant acids. These radicals have a chance to react with ROH instead with oxygen. Such a reaction breaks the chain and renders the complexes unable to proceed with photosynthesis until ROH is restored. Thus short lived complexes are formed which are unable to use the light absorbed for photochemical purposes and are thus strong reemitters of light. The production of these complexes gives the rise of the curve. The decay following the maximum is due to the consumption of the plant acids.

Biological Aspect

Of a great importance for the role of chlorophyll in the living plant is its specificity. It has, besides the absorption in the red, also regions of absorption in the blue and in the ultraviolet, so that it can make use of a much wider range in the spectrum. But if these much larger quanta could be used directly for photochemical reactions, such reactions, involving much higher energies, could be destructive for the plant. Therefore a mechanism must be present by which only an energy corresponding to $\lambda = 660\mu m$ is used for photochemical reactions, even if such larger quanta are absorbed. Recently Teller[22] has shown how that is possible for polyatomic molecules. If a molecule is brought into a highly excited state, it may drop back quickly into the lowest excited state without radiation, the difference of energy going over into vibrational energy and being conducted away as heat. From the lowest excited state, it can either go back into the normal state under the emission of fluorescence or react photochemically.

While we do not know why chlorophyll has this property, it is shown that it does have it, by the fact that the color of its fluorescence is always red, even if excited by yellow-green or blue light.

The proposed chemical mechanism permits us to understand how the plant is protected in another manner. The back reactions which we discussed in the chapter on photosynthesis protect the plant from too large a rate of photosynthesis if the light intensity becomes too high; otherwise too much aldehyde would be produced (overfeeding).

Similarly, if there is too little CO_2 present, the products of respiration (the plant acids) can be photosynthesized and this play between the products of photosynthesis and photo- and catalytic oxidation prevents an attack on the main structure of the plant. Only a long intense illumination in the absence of CO_2 would lead to a photooxidation of the main material of the plant, just as only with long starvation of an animal the vital parts are attacked.

In conclusion, we wish to express our thanks for the many helpful criticisms and suggestions we have received in the course of discussions. For these we are indebted to many scientists among them especially to Dr. Dean Burk of the Fixed Nitrogen laboratory, and to Dr. A. Corwin, chemistry department of the Johns Hopkins University.

[22] E. Teller, J. Phys. Chem. **41**, 109 (1937).

The Primary Oxide Film on Iron

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The identity and structure of the invisible, air-formed oxide film on iron has never been determined although the practical importance of a knowledge of its properties in the study of corrosion has been demonstrated. Electron diffraction experiments are now reported which show this film to be structurally identical with Fe_3O_4. In addition, it is found that the oxide has a definite orientation relationship with the underlying iron, *viz.*, the [$\sqrt{2}$10] directions in the oxide crystals are parallel to the [111] directions in the iron. Freshly abraded surfaces of electrolytic and ingot iron were investigated. Evaporated films of electrolytic iron were prepared in the diffraction camera and pictures taken before and after exposure to air show that Fe_3O_4 forms rapidly in dry air at room temperature. An air pressure of 10^{-3} mm for a few minutes gave a measurable effect. Exposure to air at atmospheric pressure for periods longer than a few minutes does not greatly strengthen the oxide pattern. The factors affecting the sensitivity of this method of examining thin films on metals are discussed.

INTRODUCTION

THE existence of an air-formed oxide film on freshly cleaned iron surfaces has been suspected for a long time. Because a knowledge of the structure and properties of such a film is of practical as well as fundamental importance, a number of investigations have been undertaken during the last ten years. Vernon[1] demonstrated the practical effect of the primary oxide film in retarding the corrosion rate of iron. He found that clean iron exposed to filtered air acquired an invisible protective film which greatly diminished the rate of rusting when exposed to ordinary atmospheric air. Freundlich, Patscheke and Zocker[2] used optical methods to study the effect of air on iron mirrors prepared by the thermal decomposition of iron carbonyl. Mirrors prepared in a vacuum displayed considerable chemical activity but on exposure to air for less than 10 sec. they acquired a passivity which was not lost on reevacuation to pressures of 10^{-4} mm. They concluded that the passivity was the result of an oxide film about 10A thick. More recently Tronstad and Höverstad[3] have made optical measurements on polished iron surfaces which they conclude are covered with a natural oxide film at least 20A thick. Using gravimetric methods, Vernon[4] found that the oxide film formed by heating in air below 200°C is structurally different from that formed at higher temperatures. Electron diffraction pictures substantiated this conclusion and gave Fe_2O_3 for the high temperature form and Fe_3O_4 for the oxide formed on heating at temperatures below 200°C.

No one has reported the application of electron diffraction to the study of natural oxide films on iron, but the method has been used successfully by Steinheil[5] and Beeching[6] to detect air-formed oxide films on evaporated aluminum, by Riedmiller[7] on evaporated nickel, and by Finch and Quarrell on zinc.[8] Since there is reason to believe that the natural oxide film is somewhat thicker on iron than on any of these metals, it seemed likely that the method might be successfully applied to iron. Moreover, electron diffraction pictures of freshly cleaned pieces of fairly pure iron exhibited extra bands which could not be attributed to impurities and which suggested the presence of an oxide film. The present work was undertaken, therefore, to study the structure of the primary oxide film formed on evaporated iron when exposed to dry air at room temperature, and to compare the results with the diffraction patterns observed on massive iron.[9] Although some of the samples were heated in air to moderate temperatures, no attempt has been

[1] W. H. J. Vernon, Trans. Faraday Soc. **23**, 159 (1927).
[2] H. Freundlich, G. Patscheke and H. Zocker, Zeits. f. physik. Chemie **128**, 321 (1927); **130**, 289 (1927).
[3] L. Tronstad and T. Höverstad, Zeits. f. physik. Chemie **170**, 172 (1934).
[4] W. H. J. Vernon, Trans. Faraday Soc. **31**, 1670 (1935).
[5] A. Steinheil, Ann. d. Physik **19**, 465 (1934).
[6] R. Beeching, Phil. Mag. **22**, 938 (1936).
[7] R. Riedmiller, Zeits. f. Physik **102**, 408 (1936).
[8] G. I. Finch and A. G. Quarrell, Proc. Phys. Soc. **46**, 148 (1934).
[9] A preliminary announcement of some of these results has appeared in Nature **139**, 30 (1937).

made to follow structural changes as a function of time and temperature. Heating was used simply as an auxiliary process to aid in the analysis of films formed at room temperature.

This investigation is a part of a general program designed to discover and develop useful metallurgical applications of the electron diffraction technique. Since the primary oxide film is the real starting point in studies of the corrosion and oxidation of ferrous materials, the present work forms an important part of such a program. The thinness of the films affords a sensitivity test of the method, and the factors which affect this sensitivity are discussed in some detail.

Experimental

The diffraction camera is similar to that described by Thomson and Fraser[10] with a hot cathode substituted for the discharge tube. Rectified and filtered a.c. provides a constant accelerating potential. Voltages of 30 to 40 kv were used with a sample-to-plate distance of 40 cm. The grazing incidence or "reflection" method was used.

The evaporated films were prepared by evaporating pieces of electrolytic iron from a small electrically heated tungsten helix placed about 8 cm from the receiving surface in the specimen chamber of the camera. Although the vacuum system was not provided with a vacuum gauge, the pressure during evaporation was 10^{-4} mm or less as estimated from a test discharge tube attached to the system. The evaporation time ranged from a few seconds to a minute or more depending on the rate and the thickness of the desired deposit. Immediately after evaporation the freshly formed film could be moved into position to take a picture after which it was necessary to open the camera in order to change plates. From 4 to 7 min. were required to raise the system to atmospheric pressure, change plates and pump down to working pressure again. The samples were at atmospheric pressure only one to two minutes, the remainder of the time being required to raise and lower the pressure. Air and other gases were always admitted to the camera through a calcium chloride drying tube. The evaporated iron was deposited on glass, quartz, iron and platinum surfaces. Various cleaning methods were used in preparing the glass and quartz plates. The simple technique of washing with soap and water, rinsing in distilled water and drying on a clean cloth seemed to be quite as effective as the more elaborate cleaning methods which were tried. No diffraction effects were detected which could be attributed to differences in the cleaning process.

Most of the massive iron samples were in the form of small rectangular blocks cut from ingot iron (Armco) of the following analysis:

	Percent
Carbon	0.02
Manganese	0.03
Phosphorus	0.019
Sulphur	0.026
Copper	0.05

A few samples were cut from annealed sheets of electrolytic iron. The specimens were cleaned by grinding all six surfaces before the final abrading process which is described in another section. Care was taken not to contaminate the surfaces with grease from the hands or other sources.

Results

Evaporated iron—random orientation

Fig. 1 is the pattern obtained from a thin iron film evaporated under conditions which give nearly random orientation of the crystallites. The trace of this plate made on a Moll recording microphotometer is reproduced in Fig. 4*A*. Immediately after this picture was taken air at room temperature was admitted to the camera through the drying tube, and plates were changed. The picture taken directly thereafter is shown in Fig. 2, and Fig. 4*B* is the corresponding microphotometer curve. Fig. 4*C* is the curve obtained after the film had been exposed to air for several hours. It is apparent that exposure to air produces two obvious changes in the diffraction pattern. In the first place the background scattering is increased causing the iron rings to appear fainter, and, secondly, new rings appear in the form of two broad bands. One of these falls well within the (110) iron ring while the other is just inside the (200) ring and is usually

[10] G. P. Thomson and C. G. Fraser, Proc. Roy. Soc. **A128**, 641 (1930).

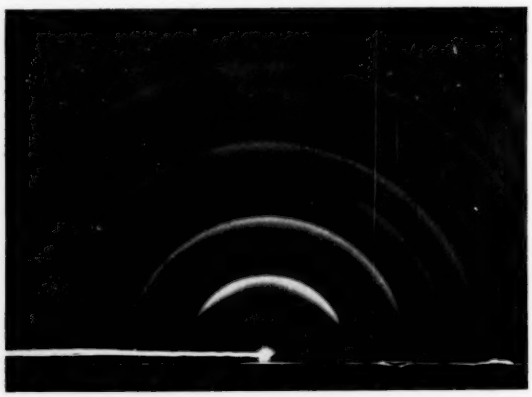

FIG. 1. Freshly evaporated film; random orientation; not exposed to air.

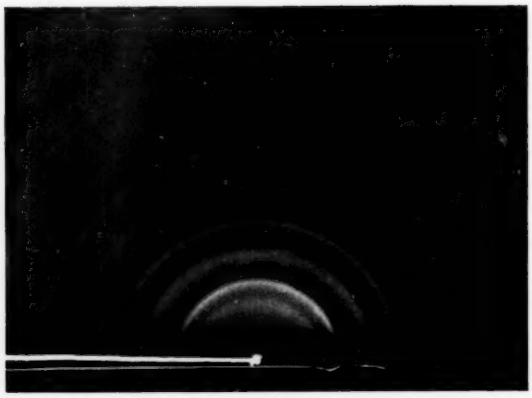

FIG. 2. Same film as Fig. 1 after exposure to air for several minutes.

not resolved therefrom. The pattern changes very little after the first few minutes of exposure to air. Over a period of a few hours there is a slight increase in the background scattering accompanied by a very slight increase in the intensity of the bands relative to the iron rings. Additional exposure to dry air up to 3 months produces no significant change.

Massive iron

If a flat iron surface is ground on successively finer grades of emery paper ending with No. 4/0, two types of surface can be obtained depending on the treatment given during the final stage. One type which we shall call an *abraded* surface is produced if the final stage consists of exerting light pressure on the sample as it is moved over unused areas of the emery paper. A different type which, for present purposes, is called a *burnished* surface is obtained if the final rubbing is carried out with greater pressure on the specimen, or if it is rubbed over used portions of the abrasive surface. Both of these processes break the surface up into successively smaller crystal fragments. The final step in the preparation of an abraded surface, however, is designed to leave the tops of ridges very thin and sharp, whereas in a burnished surface they are broad and rounded.

It is necessary, as first pointed out by Thomson,[11] that in the "reflection" type of diffraction the electrons must enter and leave the surface at the sides of ridges or projections. We would expect, therefore, that a finely abraded surface with its sharp, jagged ridges composed of fine crystal fragments will yield a better reflection pattern than will a burnished surface. This expectation has been confirmed in a large number of plates taken during the course of the present work. Severely burnished surfaces give the well-known diffuse ring pattern which has been attributed by some investigators to a surface layer of amorphous metal.[12] Less severe burnishing gives a faint iron ring pattern superimposed on an intense background. Finely abraded surfaces, however, yield fairly sharp iron rings on a relatively weak background. In addition, the patterns from finely abraded surfaces contain two diffuse rings or bands in exactly the same positions as those which appear when evaporated

FIG. 3. Abraded ingot iron.

[11] G. P. Thomson, Proc. Roy. Soc. **A128**, 750 (1930).

[12] G. I. Finch and A. G. Quarrell, Nature, **137**, 516 (1936).

films are exposed to air (see Figs. 2, 3, and 4). The microphotometer record of such a pattern from an abraded piece of ingot iron is shown in Fig. 4*D*. The similarity between this curve and those from air-exposed evaporated films is apparent.

A number of control experiments were performed to eliminate the possibility that the bands might be due to particles of abrasive left imbedded in the surface. Some abrasive deliberately left on one sample gave a very faint, spotted ring pattern whose maxima did not coincide with the bands. No trace of this abrasive pattern has been observed on lightly abraded samples.

Interpretation of the bands

Fig. 5 is a graphical representation of iron and iron oxide diffraction patterns plotted against spacings which were calculated from accepted crystal structure data. The averages of visual measurements on a number of plates from air-exposed evaporated films are given in Fig. 4*D* while plot *E* is a similar representation of patterns obtained from abraded iron. It is apparent that the observed patterns cannot be attributed to $\alpha-Fe_2O_3$ but are in good agreement with Fe_3O_4 or $\gamma-Fe_2O_3$ superimposed on the normal iron pattern.[13] The very small crystal size indicated by the lack of resolution of the strong oxide rings is discussed in a later section.

In an attempt to strengthen the oxide pattern, a number of samples were heated in air at 200°C and the changes in the film were followed by taking pictures at frequent intervals. In general when an abraded sample is heated, the iron rings fade out quickly and the bands become stronger without resolution into their component rings. The surface film first becomes visible after about 2 hrs. at 200°C and simultaneously traces of $\alpha-Fe_2O_3$ appear. Evaporated films behave similarly when heated except that usually there is a tendency for the bands to be resolved into the separate Fe_3O_4 rings before giving way to other oxide patterns.

Oriented evaporated films

During the course of this investigation, a marked tendency toward preferred orientation

[13] Fe_3O_4 and $\gamma-Fe_2O_3$ have unit cells which are identical in size, and they are virtually indistinguishable by diffraction methods.

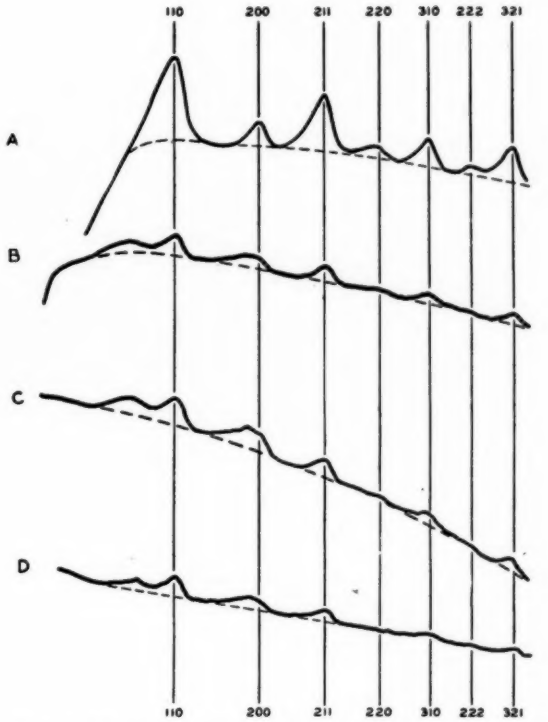

FIG. 4. Microphotometer curves. *A*, freshly evaporated film; *B*, same film after exposure to air for several minutes; *C*, after exposure for a few hours; *D*, abraded ingot iron surface.

of the evaporated films was observed. Neither the explanation of this effect nor the conditions which produce it are well understood and further work on that problem is under way.[14] For present purposes, however, it is sufficient to say that the individual iron crystals tend to orient themselves with their [111] directions parallel to the direction along which the approaching iron atoms travel. In other words the [111] directions point toward the tungsten helix from which the iron came. It has been possible, therefore, to study the air-formed oxide layer on evaporated films whose [111] directions made nearly any desired angle with the surface. We shall limit our discussion to the orientation which is simplest to interpret, *viz.*, that in which the fiber axis, [111], is perpendicular to the electron beam and to the surface of the sample. In such a case the (111) planes will be parallel to the surface, and the rings corresponding to various orders of (111) reflections will show maxima in a direction

[14] Beeching has recently found a somewhat similar effect in evaporated aluminum films. See reference 6.

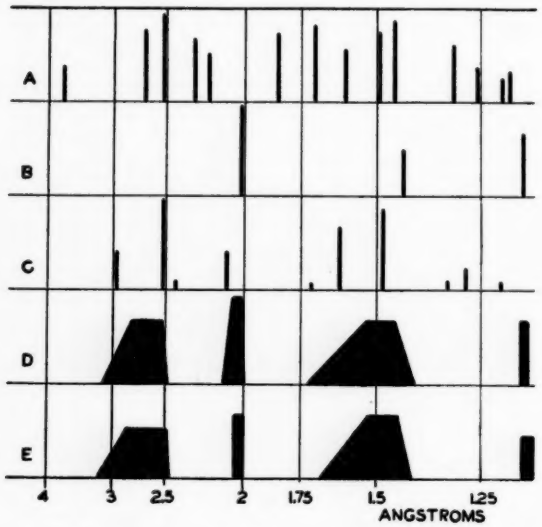

FIG. 5. Calculated and observed iron and iron oxide patterns. Calculated patterns: *A*, $\alpha-Fe_2O_3$; *B*, $\alpha-$iron; *C*, Fe_3O_4. Observed patterns: *D*, air-exposed evaporated film; *E*, abraded iron. Heights of lines indicate relative intensities.

normal to the plane of the sample. Since the Bragg angles are small ($\theta<3°$), the normal to any plane which is in a position to reflect must be very nearly perpendicular to the incident beam. It follows, therefore, that the angle ϕ measured on the plate between radii from the central spot to the maximum corresponding to the oriented plane $(h_1k_1l_1)$ and the maximum due to another plane $(h_2k_2l_2)$ is equal to the angle between these two planes in the crystal. Thus we have

$$\cos\phi=\frac{h_1h_2+k_1k_2+l_1l_2}{[(h_1^2+k_1^2+l_1^2)(h_2^2+k_2^2+l_2^2)]^{\frac{1}{2}}}.$$

Since we are dealing with cubic crystals, the indices in this equation may be considered as Miller indices of planes or as directional indices of the normals to the corresponding planes.

A pattern from an iron film oriented with [111] directions nearly perpendicular to the surface is shown in Fig. 6. All the maxima due to iron fall on well-defined layer lines which measure the distance between atoms in [111] rows. Data from the iron pattern on this plate are given in Table I. The radius, r, of the rings is given in the first column while the next two columns give a comparison between values of ϕ calculated for [111] orientation and the observed values. The agreement is well within the error of measurement. This particular picture also contains maxima which do not fall on the layer lines, in particular an intense, elongated spot between the first and second layer lines at $\phi=0$ and others inside the first layer line. These are due to air-oxidation which took place when a slight leak developed immediately after evaporation. The pressure in the camera rose to a value which probably did not exceed 10^{-3} mm for a period of not over 5 min. Immediately thereafter plate 835 was taken. The history of this particular sample is given in Table II, and numerical data from the resulting pictures are presented in Table III.

Even before heating an oriented film, the various reflections are resolved because of the different angular positions of the maxima. Consequently the two diffuse bands observed on randomly oriented films can now be separated into their component reflections, as is indicated in the first three columns of Table III. Since, however, there was no observable change in the position and relative intensities of the oxide maxima as a result of heating, it follows that the primary oxide film is identical, as regards crystalline form and orientation, with the oxide film after heating. Therefore the complete analysis of the oxide pattern as given in Table III is made from the heated film with the assurance that the results apply to the primary film.

The observed reflections and their relative intensities are in good agreement with the pattern to be expected from Fe_3O_4 or $\gamma-Fe_2O_3$. The observed value of a_0 is 8.38A as compared with the x-ray value of 8.374A.

Examination of a large number of oriented films leads to the conclusion that the oxide crystals are always oriented with the same crystallographic direction parallel to the Fe [111] direction and that this relationship is independent of the angle the Fe [111] direction makes with the surface. Inspection of the plates and an approximate calculation indicated that this direction in the oxide has the form [*hkl*] where $h/k\approx1.4$ and $l\ll h$ or $l=0$. If $l\neq0$, reflections from the form (*hhh*) would in general have 4 maxima in a quadrant instead of 2 as observed, the form (*hh*0) would show 6 maxima instead of 4, etc. Measurements on the plate cannot be made precisely enough to exclude the possibility

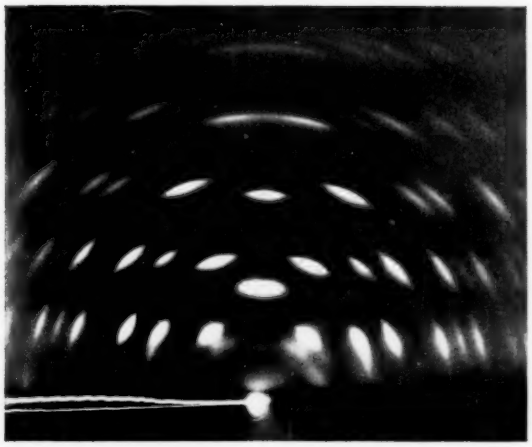

FIG. 6. Plate 835. Oriented film slightly exposed to air.

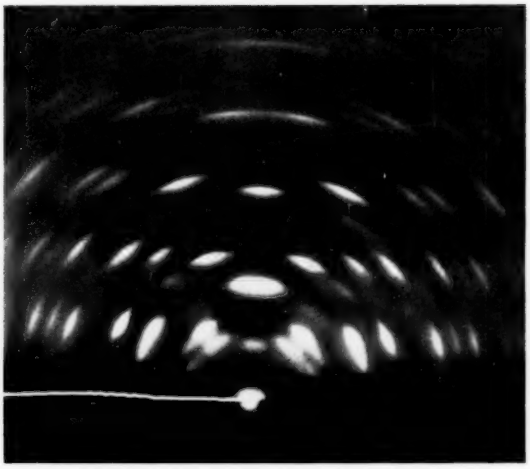

FIG. 7. Plate 836. Oriented film air-exposed for 2 min.

that l is small compared with h and k as, for example [21, 15, 1]. Since, however, there is no reason for believing the orientation relationship to be complex rather than simple, we conclude that $l=0$. Careful measurements on several plates give $h/k=1.40\pm0.05$. This includes the possibility of $[\sqrt{2}10]$ for which the values of ϕ, calculated to the nearest degree, are given in the last column of Table III. In comparing the observed and calculated values, it must be remembered that the shadow of the sample obscures maxima at large values of ϕ. The innermost reflections are cut off at about 55° while maxima on the outer rings cannot be measured accurately above 75°. If we start with a film in which the Fe [111] direction is inclined to the surface but is set perpendicular to the beam, larger values of ϕ can be measured on one side of the line of symmetry on the plate. On such plates satisfactory agreement between observed and calculated values of ϕ has been found over a complete quadrant.

Miscellaneous experiments

In order to determine the complete spacial orientation relationship by this method it would be necessary to make a film in which the iron crystals are oriented about some axis other than [111]. Attempts to obtain such a film have failed. One method which was tried consisted of electroplating a thin layer of iron onto a piece of ingot iron. The plated film was indeed highly oriented but again with [111] directions perpendicular to the surface. In every respect the oxide patterns observed on this specimen, before and after heating, were like those on the evaporated films. In this case, however, there is some doubt as to how much of the initial oxidation took place before it was dry and how much was truly air-formed.

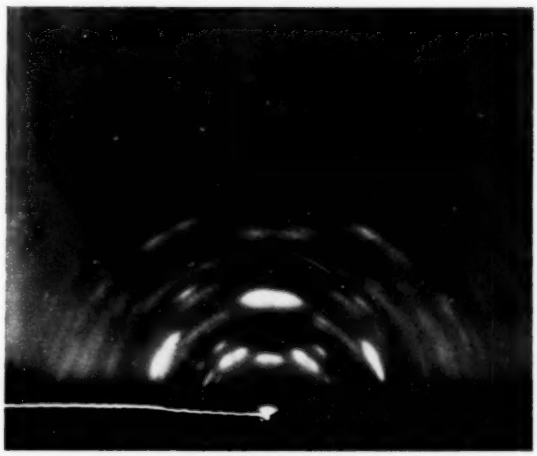

FIG. 8. Plate 839. Oriented film heated in air at 200°C for 15 min.

Most of the evaporated films were formed on glass, but some were deposited on quartz, platinum or iron surfaces. As might be expected the base has no apparent effect on the primary oxide film.

Some of the evaporated films were exposed to gases other than air. Ordinary commercial tank

hydrogen, oxygen, and carbon dioxide were used without purification. Brief exposure to any one of the three gave strong oxide patterns and no differences which could be considered significant were observed. Since oxygen is present as an impurity in both the hydrogen and carbon dioxide, it is probable that the oxygen partial pressure was appreciable during the exposure.

One transmission sample of evaporated iron, randomly oriented and 400 to 600A thick was tried. Even after exposure to air for several days there was only a faint trace of the inner oxide band.

Attempts to obtain abraded iron surfaces free from oxide films have not been successful. A sample abraded under benzene showed oxide bands exactly like dry abraded surfaces. The oxidation may have taken place during the abrading process or after the benzene evaporated. A scheme for abrading samples in the camera under a good vacuum is needed to test this point.

Discussion

Using x-rays, Mehl, McCandless and Rhines[15] have found a definite orientation relationship between crystals of FeO and the single crystal of iron on which they were grown by high temperature oxidation. Fe_3O_4 crystals which formed on partial decomposition of the FeO phase were found to be identically oriented with the FeO. The resulting orientation relationship between iron and Fe_3O_4 is therefore exactly that existing between iron and FeO which is described as follows: the cube or (100) plane in the oxide is parallel to the (100) plane in the iron; the [110] direction in the (100) plane of the oxide is parallel to the [100] direction in the (100) plane of the iron.

When any two cubic crystals have this orientation relationship, the [111] directions in one are parallel to $[\sqrt{2}10]$ directions in the other. It is apparent, therefore, that the orientation relationship between iron and the air-formed oxide is the same as that which exists between iron and cubic iron oxides formed at high temperatures. Mehl and McCandless[15] have pointed out that this orientation is reasonable on the basis of matching atomic positions in the cube faces.

The determination of particle size from the breadth of the diffraction rings is subject to many errors which could not be readily controlled. The diffraction patterns indicate that a wide range of particle sizes is involved. Neglecting geometrical and other factors which contribute to ring width, a rough calculation indicates that most of the crystals are larger than 15A. This figure is probably too small and in any case it gives no clue to the thickness of the oxide films. Finer particle sizes probably favor greater oxide penetration due to attack along grain boundaries.

The sensitivity of the electron diffraction method in detecting and examining thin films, such as these oxide films, merits consideration. The relatively low background intensity which is observed on patterns from evaporated films indicates that the surfaces must be exceedingly rough on an atomic scale with many small crystals projecting above the mean surface level in positions to yield a relatively high fraction of coherently scattered electrons. On exposure to

Table I. *Oriented iron pattern. Plate 835.*

r (cm)	ϕ observed (Degrees)	ϕ calculated [111] orientation	hkl	$h^2+k^2+l^2$	$\frac{r}{(h^2+k^2+l^2)^{\frac{1}{2}}}$
1.29	34	35 90	110	2	0.912
1.82	56	55	200	4	.910
2.22	19 62	19 62 90	211	6	.907
2.55	34	35 90	220	8	.902
2.86	43 68	43 69	310	10	.905
3.13	0 70	0 70	222	12	.904
3.38	21 52 72	22 52 72 90	321	14	.904
3.62	56	55	400	16	.905
3.84	35 57 75	57 74 35 90	411 330	18	.905
4.05	39 75	39 75	420	20	.905
4.24	7 60 76	10 60 76	332	22	.904

$\lambda = 0.0649$A: $L = 40.0$ cm: $a_0 = (\lambda L/r)(h^2+k^2+l^2)^{\frac{1}{2}} = 2.87$A: Accepted x-ray value: 2.8607A.

Table II. *History of an oriented evaporated film.*

Treatment	Plate No.	Results
Evaporated film exposed to air pressure of 10^{-3} for 5 min.	835	Strong iron pattern, highly oriented Faint oxide pattern, highly oriented
Film exposed to dry air at atmospheric pressure for 2 min.	836	Iron pattern slightly fainter. Oxide pattern much stronger. Orientation the same.
Further exposure to dry atmospheric air for 14 hrs.	837	Very little change.
Sample in air at 200° for 15 min.	839	Iron pattern completely gone. Oxide maxima stronger and sharper with orientation unchanged.

[15] R. F. Mehl, E. L. McCandless and F. N. Rhines, Nature **134**, 1009 (1934); Mehl and McCandless, Nature, **137**, 702 (1936).

TABLE III. *Diffraction data, oriented oxide film. Relative intensities: sss, very, very strong; ss, very strong; s, strong; m, medium; f, faint; ff, very faint; fff, very very faint.*

PLATE NO. 835	836	837	839						
d/n	*d/n*	*d/n*	*d/n*	Rel. Int.	a_0	ϕ Observed	$h^2+k^2+l^2$	*hkl*	ϕ Calculated [$\sqrt{210}$] Orientation
3.05	3.01	2.95	2.98	*s*	8.42	6 53—*	8	220	10 55 66 80
2.51	2.56	2.52	2.52	*ss*	8.35	24 38 53—	11	113	24 40 56 65 74 86
2.16	2.14	2.13	2.11	*m*	8.44	36 55	16	400	35 55 90
			1.72	*f*	8.42	27 35 57 62—	24	224	25 36 55 64 82 84
1.62	1.64	1.61	1.60	*m*	8.32	27 36 46 70—	27	{333 {115	36 82 26 45 48 68 74 87
1.49	1.49	1.47	1.475	*sss*	8.34	6 57 66	32	440	10 55 66 80
	1.30	1.29	1.275	*f*	8.36	27 35 52 65—	43	335	28 36 50 69 84 86
1.22	1.21	1.21	1.21	*m*	8.38	36 80—	48	444	36 82
	1.10	1.09	1.10 *m*, diffuse			Not resolved	{56 {731 {59	642 12 maxima {553	12 maxima 6 maxima
		1.04	1.045	*f*	8.35	36 54	64	800	35 55 90
	0.99	0.97	0.97	*m*	8.39	6 19 36 42 (and more)	75	{555 {157	36 82 6 20 43 (and 9 more)
			0.934	*ff*	8.36	8 27 45 60—	80	480	9 28 43 65 69 81
			0.884	*fff*	8.43		91	139	12 maxima
	0.86	0.86	0.855	*m*	8.37	26 36 56 65 80—	96	448	25 36 55 64 82 84
			Mean a_0=		8.38A				

* A value of ϕ followed by a dash indicates that the maximum is cut off by the shadow of the sample.

air, this rough surface becomes coated with a thin film of oxide. At the peaks of projections, where the oxygen can attack from all sides, very small iron crystals, 50A or less in diameter let us say, are probably completely oxidized. Since the peaks of projections are most likely to be hit by grazing incidence electrons, the oxide scatters with a high degree of efficiency. Lower down, where the projections are thicker in a direction parallel to the surface, the electrons must traverse a thin film of oxide followed by a core of iron, which may be ten or more times as thick, before again emerging through a thin film of oxide. Most of the electrons singly scattered in such a path will be scattered by the iron. An air-exposed evaporated film, therefore, should be expected to give strong oxide reflections superimposed on an iron pattern which has been considerably weakened by the exposure to air.

A finely abraded iron surface approaches the condition described above, but it is undoubtedly much coarser with broader peaks and consequently less opportunity for electrons to traverse oxide alone. On burnished surfaces the ridges are even more flattened and there is still less chance that an electron will be scattered by the oxide film alone. It is also possible that some of the electrons strike the flattened tops of ridges at such small glancing angles as to suffer appreciable refraction.[16]

These considerations lead to the conclusion that thin films on polished or burnished metal surfaces cannot be detected or examined by reflection methods as readily as can the same films on surfaces which are rough on a submicroscopic scale. Any method by which the roughnesses can be made finer will enhance the possibility of detecting a film. The sensitivity of the transmission method, on the other hand, is limited by the difficulty of preparing sufficiently thin metal films. It is difficult to mount films less than a few hundred angstroms thick. An oxide layer 30A thick covering the surfaces of such a film would give a relatively weak pattern.

[16] G. P. Thomson, Phil. Mag. **18**, 640 (1934).

On the Boiling Points of Organic Compounds. I. The Formula of Boggia-Lera

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(Received, January 6, 1937)

ALTHOUGH the boiling point of the more complicated compounds, such as those we usually find among organic substances, depends on a number of different properties of the molecule, the exceptional practical importance of this quantity makes it worthwhile to establish empirical methods for calculating its value. Our starting point will be the fact, which was discovered by Young,[1] that the increase of the boiling point per CH_2 group in different homologous series is determined by the boiling point of the substance to which the methylene group is added alone, independently of its structure and composition. This rule, which holds with surprising accuracy except in the case of associated liquids like acids or alcohols, was expressed by Young in the following formula, in which Δ_T indicates the increase in boiling point on the introduction of one CH_2 group and T_B the boiling point in degrees absolute.

$$\Delta_T = \frac{144.86}{T_B^{0.0148\sqrt{T_B}}}. \tag{1}$$

Young remarks that this formula does not apply to the first members of a series; it can only be used for compounds which contain the configuration $-C-C-C-$. As we shall make use of the fact, that Δ_T is determined by T_B, we shall have to restrict ourselves to substances which contain three carbon atoms. It is clear that the Young formula cannot be used to express the boiling points of an entire series in one mathematical expression, which makes its application very cumbersome.

For this reason we shall go back to a formula proposed by Boggia-Lera[2] for the monoderivates of the paraffin series. It says that the square of the boiling points of a homologous series expressed in degrees Kelvin form a linear function of the molecular weight, or, which is the same, of the number of CH_2 groups. We shall write this formula:

$$T = (n \cdot D + B)^{\frac{1}{2}}, \tag{2}$$

n being the number of CH_2 groups in the molecule, D and B are constant in a given series. From the fact that the increase of T with n is dependent on T only, one easily concludes that D must have the same value for every homologous series. This is not exactly what Boggia-Lera found, but the variation in his values of D is small, and besides it is seen from the consideration of a series in which a great number of boiling points are known, like the paraffins, that D is not quite constant, and that therefore the value computed depends more or less on the number of substances considered. Table I[3] shows that the value $D=20{,}500$ fits most of the paraffins and their monoderivates quite accurately. Only the highest members of the paraffin series show considerable deviations. The calculated values for the boiling points of molecules which do not contain the configuration $-C-C-C-$ are shown between brackets; in most of these cases the agreement is very poor, the paraffins and alkylhalides being exceptions. It must be specially pointed out, that the reasons for the validity of our empirical formula (2) are various and of a complicated nature. We hope to deal with these theoretical considerations in a later paper but in this connection we want to stress the fact that we have no reason to assume that our formula will hold with any accuracy outside the range for which we have ascertained its validity.

After proving the applicability of formula (2) with the value 20,500 for D in the case of monoderivates of paraffins we must investigate whether it can also be used for other compounds. Adequate data are available for paraffin derivates bearing a group at each end and for those having a substituent in the middle. In both cases our

[1] Young, Phil. Mag. **9**, 1 (1905).
[2] E. Boggia-Lera, Gazz. chim. Ital. **29**, 1, 441 (1899).
[3] The data are taken from Beilstein and from Wakeman, Rec. **53**, 832 (1934).

formula applies, within the limitations mentioned before, as shown in Tables II and III.

Now the only matter left for consideration is the value of the constant B in different series. As all series considered in Table I and II are different only in the end groups, it is logical to ascribe to these end groups the differences in B. It is found that the values for this constant are roughly additive as a function of the two end groups. If we take the value for H as one-half of the B in the paraffin series, we can calculate all B's for the substances in Table I. In Table IV the values found in this way, marked I are compared to the values found by halving the con-

TABLE I. $T=(n\cdot 20{,}500+B)^{\frac{1}{2}}$.

	Paraffins $H(CH_2)_nH$ $B=-7000$		Olefines $H(CH_2)_n-CH=CH_2$ $B=31000$		Alkyl-acetylenes $H(CH_2)_n-C\equiv CH$ $B=40000$		2-methyl Paraffins $H(CH_2)_n-CH(CH_3)_2$ $B=49500$		Methyl-alkyl-acetylenes $H(CH_2)_n-C\equiv C-CH_3$ $B=67000$		Alkyl-monochlorides $H-(CH_2)_nCl$ $B=41000$	
n	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T
1	(116)	112	227	225	246	250	264	263	296	301	(248)	249
2	(184)	185	268	268	285	291	301	304	329	328	(286)	285
3	233	228	304	303	319	313	333	334	358	359	320	320
4	274	274	336	337	349	344–345	363	363	386	386	351	351
5	309	309	365	367	377	373	390	390	412	411	379	379
6	341	342	392	394–395	404	400–401			436	434	405	407
7	370	371	418	419	428	424–425					453	458
8	397	398	442	441								
9	421	424	464	461–463								
10	445	447										
11	467	470										
12	489	489										
13	509	507										
14	530	525										
15	548	543										
16	567	560										
17	584	576										
18	602	590										
19	618	603										

	Alkyl-monobromides $H(CH_2)_nBr$ $B=57500$		Alkyl-monoiodides $H(CH_2)_nI$ $B=80500$		Methyl Ethers $H(CH_2)_nOCH_3$ $B=35500$		Alkyl Formates $HCOO(CH_2)_nH$ $B=62000$		Methyl Esters $H(CH_2)_nCOOCH_3$ $B=79000$		Mercaptans $H(CH_2)_nSH$ $B=55000$	
n	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T
1	(279)	278	(318)	316	(237)	248	(287)	305	(315)	330	(275)	279
2	(314)	311	(349)	345	(277)	284	(321)	327	347	353	(310)	310
3	345	344	377	375	312	312	351	354	375	375	341	340
4	374	364?	403	400	343	344	379	380	401	400	370	370
5	400	403	428	429	372	372–373	406	403	426	423	397	399
6	425	429	451	453			430	427	449	446	422	420
7					423	423	453	450	472	466	447	447
8			494	498	447	446	475	471	493	486–487		
9									513	496–497		
10												
11												
12												
13									579	568		
14												
15												
16												
17									646	715–716?		

TABLE II. $T=(n\cdot 20{,}500+B)^{\frac{1}{2}}$.

	DIMETHYL PARAFFINS $(CH_3)_2CH(CH_2)_n-CH(CH_3)_2$ $B=105000$		ALKYL DICHLORIDES $Cl(CH_2)_nCl$ $B=100000$		ALKYLDIBROMIDES $Br(CH_2)_{n2}Br$ $B=137000$		DIMETHYL ETHERS $CH_3O(CH_2)_nOCH_3$ $B=81000$		DIMETHYL DICARBOXYLESTERS $CH_3OOC(CH_2)_n-COOCH_3$ $B=17700$	
n	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T	T_{calc}	T
1	354	358–359	(347)	313	(397)	371	319	318	444	454
2	382	382	(375)	357	(422)	404	349	~355	467	465
3	408	406	402	398	446	441			488	487
4	432	433	427	434–436?	468	470–471	404	405–406		
5			450	453	489	493–495	428	429–432		
6			472	476–478	510	512–514	453	453	547	541
7					530	536	473	474		
8							495	494		
9			514	513–515						
10			533	531–535						

stants used in Table II (which are marked II), and the average values are shown between brackets. Insofar as this additivity holds we can state the following rule:

"The square of the boiling points of an organic compound consisting of a chain of at least 3 carbon atoms with two end groups is an approximately additive quantity, which can be calculated by adding a certain characteristic value for each methylene and end group." In Table V the boiling points for a number of compounds are calculated from this rule.

Formula (2), although it is not quite exact, can help us to information about the so-called "replacement values" of boiling points; the change which occurs in the boiling points of a substance on substitution of one group for another. Smiles[4] remarks on the fact that such a "replacement value" decreases with increasing term number and expresses the opinion that it may ultimately become constant. From our formula we are indeed led to expect a constant difference between the squares of the absolute boiling points, which means that the difference between the boiling points of two compounds

TABLE III. $T=(n\cdot 20{,}500+B)^{\frac{1}{2}}$.

	METHYL PARAFFINS $H(CH_2)_{n/2}-C(CH_3)(CH_3)_{n/2}H$ $B=28000$		DIALKYLETHERS $H(CH_2)_{n/2}O(CH_2)_{n/2}H$ $b=8000$	
n	T_{calc}	T	T_{calc}	T
2	265	263	(221)	249
4	333	337	(300)	308
6	390	391	362	364
8	439	438	415	414
10				
12			543	535
14			580	565

[4] Smiles, *Chemical Constitution and Physical Properties*, p. 225.

TABLE IV.

END GROUP	B VALUE
H	−3500
$-CH=CH_2$ I	34500
$-C\equiv CH_2$ I	43500
$-CH(CH_3)_2$ I	53000
II	52000
	(52500)
$-C\equiv C-CH_3$ I	70500
−Cl I	44500
II	50000
	(47000)
−Br I	61000
II	68500
	(64500)
−I I	84000
$-OCH_3$ I	39000
II	40500
	(39500)
−OOCH	65500
$-COOCH_3$ I	82500
II	88500
	(85500)
−SH	55000

with the same term number is inversely proportional to the sum of the two boiling points. Thus the replacement value does decrease with increasing term number, but can never reach a limiting value, so long as formula (2) holds.

TABLE V.

MOLECULE	T_{calc}	T
$Cl(CH_2)_3Br$	417	415
$Cl(CH_2)_3OCH_3$	385	384
$Br(CH_2)_3OCH_3$	407	405
$I(CH_2)_3OCH_3$	430	431
$CH_3O(CH_2)_3COOCH_3$	432	436
$Cl(CH_2)_3COOCH_3$	441	436–439
$Br(CH_2)_3COOCH_3$	460	459–460
$I(CH_2)_3COOCH_3$	481	471–473
$(CH_3)_2CH(CH_2)_2Cl$	375	373
$(CH_3)_2CH(CH_2)_2Br$	397	392
$(CH_3)_2CH(CH_2)_2I$	421	420
$(CH_3)_2CH(CH_2)_3Cl$	401	398–399
$(CH_3)_2CH(CH_2)_3Br$	422	316–320
$(CH_3)_2CH(CH_2)_2CH=CH_2$	358	358
$(CH_3)_2CH(CH_2)_3CH=CH_2$	385	384–388
$CH_2=CH(CH_2)_2CH=CH_2$	332	332
$(CH_3)_2CH(CH_2)_2C\equiv CH$	370	365–366
$CH_2=CH(CH_2)_2C\equiv CH$	345	343
$CH\equiv C(CH_2)_2C\equiv CH$	358	359
$CH_2=CH(CH_2)_2OCH_3$	339	341–342
$(CH_3)_2CH(CH_2)_2OCH_3$	365	364
$(CH_3)_2CH(CH_2)_2OOCH$	399	396
$(CH_3)_2CH(CH_2)_3COOCH_3$	447	440
$(CH_3)_2CH(CH_2)_2SH$	385	389–393

TABLE VI. *Cycloparaffins* $(CH_2)_n$. $T=(n\cdot 24{,}300-18{,}000)^{\frac{1}{3}}$.

n	T_{calc}	T
3	234	238
4	286	284–285
5	322	323
6	358	353
7	390	392
8	420	422
9	448	444
10	474	474

Finally, we must point out that the cycloparaffins cannot be expected to show the same dependence of Δ_T on T_B as the paraffins and their derivates do, because the position of the hydrogen atoms towards each other is quite different in both classes of compounds. In the very large rings where all atoms can move freely the ring compounds may follow the same formula as the straight chains do, but to the cases for which we now know the boiling points the value B 20,500 does not apply. We obtain satisfactory results however if we use $B=24{,}300$, as is demonstrated in Table VI.

The Properties of Paraffins. II

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The square root in the formula of Boggia-Lera is derived in the case of the paraffins from Langmuir's ideas about the process of evaporation of liquids and van Laar's and van Arkel's rules about cohesion in liquids, combined with empirical expressions for the critical constants.

In Part I we have investigated the validity of the formula of Boggia-Lera and extended its applicability to all polymethylene compounds. The formula was originally given as a purely empirical one and up to now we have used it as such. It is, however, desirable to ascertain its causes as these may give us some information about the limits of its applicability. The boiling point of a compound is a derived quantity, depending in a complicated way on a great many different properties, among which the heat of vaporization is by far the most important. For this reason we shall check our conclusions by comparing them with the known data for the paraffins, the only homologous series for which vapor pressure measurements are available. Another advantage of these compounds is the absence of large substituents or of appreciable electrical moments, as these might have a complicating influence on the thermal properties in the series. Table VII contains the data obtained by different investigators and the values we calculated from them. For our purposes we are not so much concerned with the absolute values of the heat of vaporization as with their differences. For this reason we calculated the average value for each compound between 11 mm and 760 mm pressure, these being the lowest and the highest pressure used by Krafft. The average values for the heat of vaporization are listed under Q_{av}. From these the heats of vaporization at the boiling point were obtained by the use of the well-known formula:[1]

$$Q=Q_0(1-T/T_c)0.4, \qquad (1)$$

in which Q is the heat of vaporization and T_c the critical temperature, all temperatures being expressed in the absolute scale. The heat of vaporization at the boiling point was obtained by multiplying Q_{av} with the average of unity and the factor required to change the value of Q at 11 mm pressure to Q at the boiling point (Q_B), as calculated from formula (1). As this correction amounts to about 10 percent it is clear that the inaccuracy it introduces into Q_B is quite small.

To get an insight into the factors which determine the values of Q_B we must first consider what is known about the heat of vaporization of small and simple molecules. van Laar[2] has pointed out that for the attraction between two molecules only those atoms are important which are on the surface of the molecule. Atoms inside a molecule—like the carbon atom in CH_4 or CCl_4—which are entirely surrounded by other atoms, are screened off so effectively that one need not take them into account when calculating cohesion forces. A great deal of work on this subject has been done by van Arkel and his co-workers,[3] who studied a great variety of substances and lately even calculated the degree of screening quantitatively in some cases. In the case of larger molecules screening certainly will have the same effect, and in our case too, only those atoms of the paraffin molecule which are lying in the surface of the molecule can contribute to the intermolecular forces. This gives the three following variables on which the heat of vaporiza-

[1] R. M. Winter. J. Phys. Chem. **32**, 576 (1928). The same formula had already been used in a special case by Prud'homme (J. de. chimie physique **21**, 461 (1924)) with a different exponent. An expression of the same kind was given by van Laar for the internal heat of vaporization (*Zustandsgleichung von Gasen und Flüssigkeiten* p. 263). At higher temperatures formula (1) is quite accurate, but at very low pressures the agreement is not so good (Taylor and Smith, J. Am. Chem. Soc. **44**, 2457 (1922)). This might be due to the method of calculation however.

[2] J. J. van Laar, *Zustandsgleichung von Gasen und Flüssigkeiten*, p. 199.

[3] A. E. van Arkel, Rec. **51**, 1081 (1932); A. E. van Arkel and S. J. L. Snoek, Rec. **52**, 719 (1933); A. E. van Arkel Rec. **52**, 733 (1933); **53**, 246 (1934) and specially Chemisch Weekblad **31**, 470 (1934).

tion depends: 1. the composition of the surface of a molecule, 2. the size of the surface of a molecule, 3. the distance between the surfaces of two molecules.

The first factor does not give us any trouble with the paraffins. Because the composition of all paraffins is the same (except for the two final hydrogen atoms, which we may well neglect) the composition of their surface will be the same too. It may be that all the atoms causing the cohesion are hydrogen atoms, or there may be carbon atoms among them, but their proportion will be constant throughout the series, excepting the very first terms.

The shape of a molecule in a liquid is very complicated and irregular. Langmuir[4] has given a great deal of consideration to this problem, paying special attention to the paraffin molecules. He points out that owing to the rotation around the C−C bonds the molecule can assume a great many different shapes. Whether it does so depends on the forces between its different parts. In the gas phase the attraction between the different methylene groups is so great that the molecule will roll up into something approaching a sphere. In the liquid phase on the other hand, a group in the center of a rolled up molecule finds itself surrounded by the same methylene groups which adjoin it when it is stretched out between other molecules. Thus it takes no energy to change the shape of a molecule in a liquid consisting of the same kind of molecules and under these circumstances a molecule is not all curled up but only slightly curved. Kuhn has lately published several papers on this subject.[5]

Langmuir's conclusions are, of course, only approximately true as a methylene group in a certain molecule will more frequently turn its carbon atom towards a point inside a molecule and its hydrogen atoms towards a point outside.

It is clear that when a molecule evaporates its shape changes gradually as it moves out of the liquid into the gas phase. This process we cannot describe but the energy required for it is the same as that which must be supplied to give the molecule first the shape of a gaseous molecule in the liquid—which requires no energy—and afterwards transferring this—nearly spherical—mole-

TABLE VII.

Substance	Formula C_nH_{2n+2} Value of n	Temperature at Which $p=11$ mm in Degrees Abs.	Boiling Point in Degrees Abs.	Q_{av} in Cal.	Q_b from Gas and from (1) in Cal.	U_B in Cal.	$\frac{T_B{}^0}{T_c}$	U_{red} for $T=0.716\,T_c$ in Cal.	U_{red} Calc. from (2) $1900\times n^{\frac{2}{3}}$ in Cal.	$\frac{Q_B}{T_B}$	$\frac{Q_B}{T_B}$ Calc. from $16.0\times n^{0.14}$
Propane[a]	3	161	229	4600	4200	3700	0.619	3300	4000	18.3	18.7
Butane[a]	4	194	273	5600	5200	4700	0.640	4300	4800	19.0	19.4
Pentane[b]	5	225	310	6900	6300	5700	0.658	5300	5500	20.3	20.0
Hexane[c]	6	249	342	7700	7100	6400	0.673	6000	6300	20.8	20.6
Heptane[d]	7	273	372	8600	7900	7200	0.689	6900	7000	21.2	21.0
Octane[e]	8	294	399	9200	8600	7500	0.701	7600	7600	21.6	21.4
Nonane[f]	9	313	423	10100	9200	8400	—	8300	8200	21.8	21.7
Decane	10	330	446	10600	9700	8800	0.716	8800	8800	21.7	22.1
Undecane	11	347	468	11300	10300	9400	—	9400	9400	22.0	22.4
Dodecane	12	364	488	12000	10900	9900	—	9900	10000	22.4	22.6
Tridecane	13	379	507	12600	11400	10400	—	10400	10500	22.5	22.9
Tetradecane	14	396	526	13400	12300	11200	—	11200	11000	23.4	23.1
Pentadecane	15	410	544	13900	12700	11600	—	11600	11500	23.4	23.4
Hexadecane	16	424	561	14600	13300	12200	—	12200	12100	23.7	23.6
Heptadecane	17	437	576	15200	13900	12700	—	12700	12600	24.2	23.8
Octodecane	18	448	590	15600	14300	13100	—	13100	13000	24.2	24.0
Nonadecane	19	459	603	16100	14700	13500	—	13500	13500	24.4	24.2

[a] Values from Burrel and Robertson, J. Am. Chem. Soc. **37**, 2188 (1915). Partly interpolated.
[b] Values from Young, J. Chem. Soc. **71**, 446 (1897). The temperature at which $p=11$ mm is extrapolated, causing the figures for this substance to be less reliable. The boiling point is interpolated.
[c] Values from Thomas and Young, J. Chem. Soc. **67**, 1075 (1895). Interpolated.
[d] Values from Young, J. Chem. Soc. **73**, 675 (1898). Interpolated.
[e] Values from Young, J. Chem. Soc. **77**, 1145 (1900). Interpolated.
[f] Values for nonane and higher hydrocarbons from Krafft, Berichtr. **15**, 1145 (1882).
[g] Values for T_B and T_c from van Laar, *Zustandsgleichung von Gasen und Flüssigkeiten*, p. 184. It has been assumed that the value for decane is also valid for the higher terms of the series.

[4] I. Langmuir, in Alexander, *Colloid Chemistry I*, p. 525, and Third Colloid Symposium Monograph, p. 48 (1925).

[5] W. Kuhn, Kolloid Zeits. **68**, 2 (1934); Zeits. f. physik. Chemie **A175**, 1 (1936).

cule to the vapor. Langmuir tried to obtain a quantitative value for the heat of vaporization in this way, but that cannot be done. The internal heat of vaporization should be equal to the product of the surface of a molecule and the internal surface energy multiplied by the Avogadro number. There might be some doubt about the area of the surface of a molecule but at least the internal heat of vaporization should be proportional to the internal surface energy, except for a very small change due to the expansion of the liquid. This is by no means the case, as was shown by Whittaker.[6] There can be little doubt, however, that the internal heat of vaporization of a paraffin is actually proportional to the surface of a molecule in its spherical shape if at least the distance between the surface of the molecule and that of the surrounding liquid is the same. (It is, of course, impossible to define exactly what should be considered to make up the surface of a molecule in a liquid, especially of one which is in a rolled-up state, which occurs hardly at all in the liquid, but we shall have to use the notion all the same.)

If all methylene groups in the liquid were entirely free to move independently, the average distance between two of them would always be the same in different liquids at a certain temperature. In a molecule, however, the methylene groups are only partially free to move and therefore two CH_2 groups in different molecules will be nearer to each other the larger the molecules are to which they belong, because the attraction between the other methylene groups tends to bring the groups under consideration nearer together too. So the temperature at which the distance between a molecule and the surrounding surface has a certain value, will be higher the larger the molecular weight is. At present it seems most logical to compare different substances at corresponding temperatures, which means, temperatures that are the same fraction of the critical temperature. That is usually done and it can easily be shown to be right in the simplified case of straight, cylindrical molecules lying parallel, with no free space at the ends, as follows:

From the fact that the molecular volume of paraffins at the boiling point (which is approximately a corresponding temperature as seen from Table VII) is an additive property it follows that the intermolecular spaces make up a constant fraction of the total volume. If we increase the molecular weight the molecules only grow longer, without changing their other dimensions. The intermolecular spaces also change their total volume and their length in the same proportion, so the distance between two molecules remains the same.

The surface of a large, spherical molecule is proportional to the two-thirds power of its volume and, in the case of a paraffin, of its number of methylene groups (neglecting the final hydrogen atoms again). Thus we expect the internal heat of vaporization for different paraffins at a certain reduced temperature to be:

$$U_{\text{red}} = \text{const.}\ n^{\frac{2}{3}}. \qquad (2)$$

In Table I M_{red} is calculated for $T = 0.716 T_c$ from U_B by the use of formula (1) for comparison with the results obtained from formula (2) taking the constant to be 1900. It was assumed that the ratio of T_B and T_c was the same for decane and all the higher terms. This is certainly not true but the difference in U_{red} is probably only about 200 cal., which is not more than the error of the figures anyway. Considering that $Q = U + RT$ and that the power of U changes slightly if we make our comparison at the boiling points—which are not strictly corresponding temperatures—we get:

$$Q_B = \text{const.}\ n^{0.64}. \qquad (3)$$

The change in U caused by the change in temperatures is quite small, and can be expressed as a factor representing a small power of n. Here the constant has the value 2250.

Now we still have to convert our formula for Q_B into one for T_B. The only exact way of connecting these two quantities is by the third law of thermodynamics, but for this method we do not have the required thermal data at present, nor do we know how to apply this law to large molecules. It is, however, a well-known fact that in general the Trouton quotient increases as a function of the boiling point. In our case we may expect this to be true too, and it would mean

[6] Whittaker. Proc. Roy. Soc. **81**, 21 (1908). The same fact disproves the correctness of the formula of Stefan. (W. D. Harkins and L. E. Roberts, J. Am. Chem. Soc. **14**, 653 (1922).

that this quotient would be a function of n. The quotient changes only a little over our entire series and we may very well write it as a small power of n:

$$Q_B/T_B = 16.0 \cdot n^{0.14}. \quad (4)$$

Combining this with formula (3) we obtain as our final conclusion that T_B is proportional to the 0.50 power of n. Here we see the square root from the formula of Boggia-Lera come in more or less accidentally as the difference between two other powers of n.

It is also possible to give a proof for the value of the exponent in formula (4). Lacking the data needed for the use of the heat-theorem one has to use empirical expressions for the critical quantities. Although the factor A in the general vapor pressure equation

$$\ln p = -A/T + B \quad (5)$$

is not a constant, one may consider it to be one without introducing more than a very slight error, if one limits oneself to comparing the critical point and the boiling point; at least in the case of ordinary compounds like the paraffins.[7] This means that we can replace A by Q_B/R and by substituting p_c and T_c, find

$$Q_B/T_B = Q_B/T_c + R \ln p_c. \quad (6)$$

Now we must express the critical quantities as functions of n in a suitable way. We shall use $T_c = 251 \times n^{0.39}$ and $\ln p_c = 4.54/n^{0.17}$. We might of course have made use of the fact that T_c/p_c is proportional to the critical volume and therefore to n, thus expressing p_c in T_c and n, but this would have complicated our calculations appreciably. Combining with formula (3) we find:

$$Q_B/T_B = 8.97 \times n^{0.25} + n^{8.99/0.17}. \quad (7)$$

[7] van Laar, reference 2, p. 230.

The value of the first term on the right side of (7) increases slowly with n; the value of the second term decreases. The first term, being the larger one and having the higher power in n, will outweigh the other one; so the value of Q_B/T_B is seen to increase very slowly with increasing term number. We can again try to find a product of a single small power of n to express the total value of (7), which is seen to be quite well represented by formula (4).

So we have derived the formula of Boggia-Lera for the paraffins excepting for the lowest members of the series. It is easily seen that the agreement at the beginning of the series may be greatly improved by adding a constant either to T or $n \times D$. Formula (3) could safely be extrapolated to higher values of n, but it seems very uncertain whether formula (4) could be extrapolated, as the accuracy of the empirical expressions on which it depends is very doubtful for larger molecules. For this reason it would not be safe to use the formula of Boggia-Lera for molecules with $n > 20$. These molecules are not very stable at the boiling point, however.

It is impossible to prove theoretically the validity of the formula of Boggia-Lera for other compounds, as there are not sufficient data available. We have pointed out, however, that, as a result of the formula of Boggia-Lera, the change in boiling point caused by the replacement of one end group by another one, decreases with the number of methylene groups in a molecule. Now if, on the other hand, we wish to take this former conclusion for an empirical fact, it can easily be shown to prove that for every series the term on the right side must have the same exponent and the factor next to n must have the same value. It also proves that if we want to use an additive term it cannot be added to T. Which leaves us only the original formula of Boggia-Lera, unless we want to use expressions of a more complicated kind.

The Exchange of Energy Between Organic Molecules and Solid Surfaces

Part II. Accommodation Coefficients and Specific Heats of Paraffin Hydrocarbons and the Influence of Temperature on the Accommodation Coefficients (Including Argon) at Some 10^{-6} mm (Hg) Pressure

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The investigation of the accommodation coefficients of the paraffin hydrocarbons and their relation to the specific heats reported in Part I of this series has been extended to various temperatures of the nickel surface and to various gas temperatures. The results are, within the experimental error of about 1 percent, in full agreement with the general formulae derived in Part I, by which the accommodation coefficients of the paraffins were related to their molecular weights and their specific heats. A complete summary of these relations is given at the end of this paper.

INTRODUCTION

IN Part I of this series[1] it was shown that the accommodation coefficients of the paraffin gases and vapors as measured by a molecular beam method at some 10^{-6} mm Hg gas pressure follow, for constant temperature of gas and surface, the simple relation

$$\alpha = c_1 M/(c_1 M + c_2), \qquad (1)$$

c_1 and c_2 being constants and M the molecular weight. This expression is based on the following relation which was found to exist for paraffin hydrocarbons between the accommodation coefficient α, the specific heat per mole at constant volume for the ideal gas state C_{v_0}, and the molecular weight M,

$$\alpha(C_{v_0} + R/2)/M = \text{constant}, \qquad (2)$$

R being the gas constant per mole, and on a relation between C_{v_0} and M

$$C_{v_0} = c_1 M + 1.80, \qquad (3)$$

which was derived from reliable C_{v_0} values for ethane and butane. Eq. (3) is supported by Eq. (2) inasmuch as α rapidly approaches *one* for large M, under which condition C_{v_0} increases proportionally to M. Since Eqs. (2) and (3) were verified for *mean* specific heats between 20° and 140°C, they were likewise assumed to hold for *true* specific heats in this interval. Assuming further that the relations will also hold at moderately higher and moderately lower temperatures, Eq. (3) may be used to calculate C_{v_0} for all paraffins within a wide temperature range, provided that a reference value (ethane from normal frequencies) is known for each temperature and that all lines intersect the C_{v_0} axis at 1.80, which latter condition was assumed to be true for reasons of the apparent additivity of fundamental frequencies in the paraffin series.

In the present investigation, experimental proof is offered for the correctness of the assumptions made in Part I for a temperature interval extending to a much lower temperature, thus justifying the use of Eq. (10) (Part I) at considerably lower temperatures for the calculation of the specific heats of all paraffins[2] from the known specific heat of ethane. In writing this equation in a more general form we obtain

$$C_t = M(C_t' - 1.80)/M' + 1.80, \qquad (4)$$

where C_t is the specific heat per mole of the paraffin gas considered, at constant volume, in the ideal gas state at the temperature t, and M is its molecular weight. C_t' and M' refer to ethane, the reference gas.

EXPERIMENTAL RESULTS

For reasons sufficiently explained in Part I we have omitted methane from the present measurements and have carried out the experiments

[1] Part I, J. Chem. Phys. **4**, 680 (1936) and Errata, ibid., p. 743.

[2] For special consideration of methane, see Part I.

with ethane, propane and butane. In a first series we have kept the walls of the hot wire gauges at constant temperature (20°C) and have changed the temperature of the wire from 140°C to 40°C in intervals of 20°. The experimental data are presented in Fig. 1 by the sensitivity S (i.e., galvanometer deflection per 0.1 mm Hg gas pressure in the reservoir) plotted against the reservoir pressure. The extrapolation of these curves to the pressure zero gives the values S_0 which are independent of apparatus constants, as shown in Part I, p. 682, second column.

Again it was found that for the paraffins the values for S_0 (see Part I) are proportional to the square root of the molecular weight for all temperature intervals investigated thus verifying Eq. (2) in each case. In addition argon values were taken for each temperature interval.

In a second series the Pirani gauges were immersed in a solid CO_2 cold mixture (−78.5°C) and the wires were kept at 140°C. The resulting sensitivity curves are presented in Fig. 2. The ethane curve again shows the distinct break at a reservoir pressure of about 0.1 mm Hg which was discussed in detail in Part I. It is interesting to note that the break is already less marked at the wire temperature 120°C (Fig. 1) and has disappeared at 100°C. These facts agree well with the explanation of this phenomenon given in Part I. Also in this case perfect proportionality of the S_0 values with the square roots of the molecular weights of the paraffins is obtained.

In comparing the measurements of the two series, it is possible to verify experimentally Eq. (4). It was shown in Part I that the mean specific heats of the paraffins between 20°C and

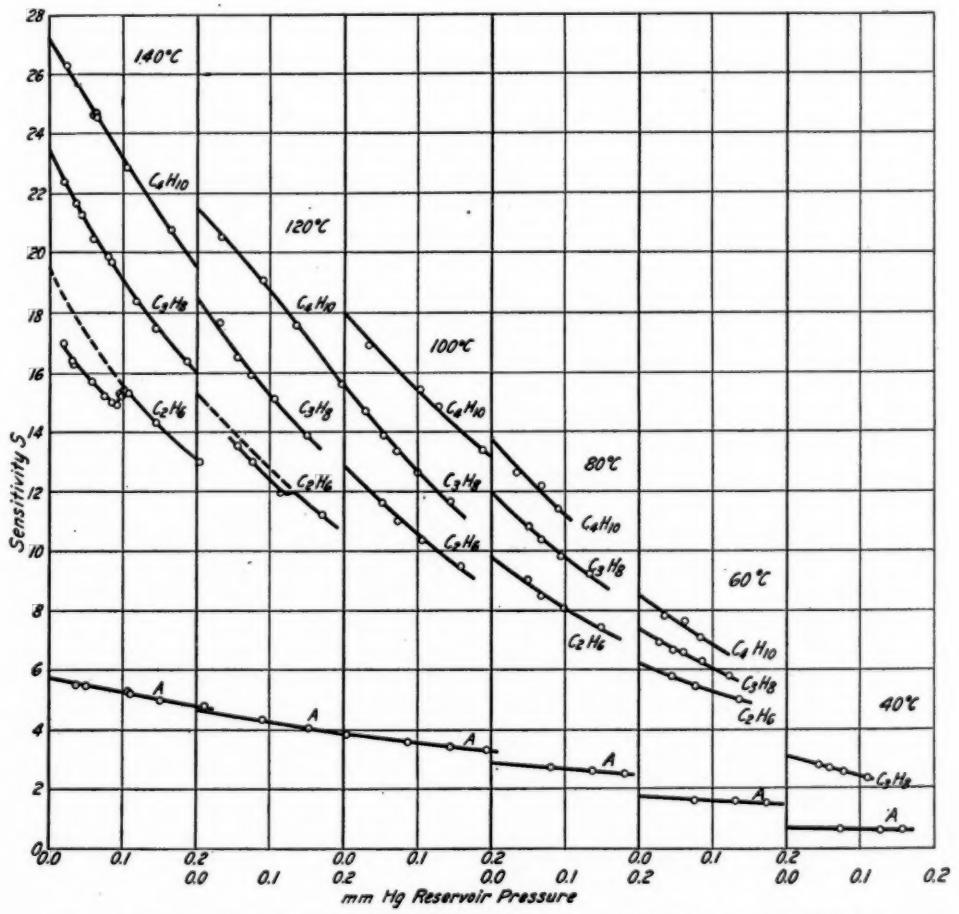

FIG. 1. Sensitivity S (i.e., galvanometer deflection per 0.1 mm Hg gas pressure in the reservoir) plotted against the reservoir pressure for various hot wire temperatures with the gauge walls at 20°C.

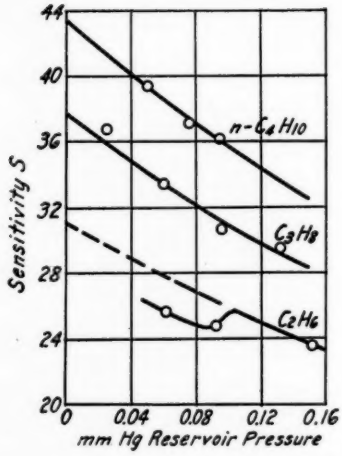

FIG. 2. Sensitivity S (i.e., galvanometer deflection per 0.1 mm Hg gas pressure in the reservoir) plotted against the reservoir pressure for the hot wire temperature of 140°C with the gauge walls at −78.5°C.

140°C may be expressed in terms of the molecular weights by the equation

$$C_{v_0(20\text{ to }140)}=0.352M+1.80$$

and α by the equation,

$$\alpha=\frac{0.352M}{0.352M+1.80+R/2},$$

or in terms of the specific heat of ethane,

$$\alpha=\frac{M(\bar{C}_{v_0}'-1.80)/M'}{M(\bar{C}_{v_0}'-1.80)/M'+1.80+R/2}, \tag{5}$$

where $\bar{C}_{v_0}'$ is the mean specific heat of ethane between the temperatures of the hot wire and the wall and M' the molecular weight of ethane.

According to Eq. (4) we obtain for the mean specific heat between −78.5°C and 140°C in terms of the specific heat of ethane

$$C_{v_0(-78.5\text{ to }140)}=\frac{(C_{v_0}'_{(-78.5\text{ to }140)}-1.80)M}{M'}+1.80, \tag{6}$$

where C' and M' again refer to ethane, the reference gas.

The mean specific heat for ethane at constant volume between −78.5°C and 140°C was calculated from normal frequencies to be 10.9 cal./mole/°C.[3]

[3] At low temperatures the inhibited rotation of the CH_3 groups was estimated according to E. Teller and K. Weigert, Nachr. Ges. Wiss. Göttingen 218 (1933).

Thus, using Eqs. (5) and (6) we find for $C_{v_0(-78.5\text{ to }140)}$ and the corresponding α:

	$C_{v_0(-78.5\text{ to }140)}$	α
Propane	15.14	0.82_7
Butane	19.38	0.86_3

In order to calculate from these data S_0 values for the temperature difference −78.5°C to 140°C from the measured S_0 values for the temperature difference 20°C to 140°C, the relative electrical sensitivity of the bridge circuit in the two cases must be known. Since the wire temperature and therefore the resistance is the same in both cases the relative current distribution through the bridge is the same in both cases and the relative sensitivity of the bridge is simply measured by changing one of the resistances by a known small fraction in both cases. In an actual experiment this change must be small enough so that the energy supplied to the wire may be regarded as constant over the experiment. A galvanometer deflection of 14.80 cm was obtained for a change of resistance in one arm by the fraction 0.01/136 in case of the temperature difference 20°C to 140°C and 15.11 cm for the same fraction with the temperature difference −78.5°C to 140°C.

By using primed symbols for the temperature difference −78.5°C to 140°C we obtain

$$S_0''=\frac{\alpha''\cdot 15.11\cdot(C_{v_0}''+R/2)(140+78.5)}{\alpha\cdot 14.80\cdot(\bar{C}_{v_0}+R/2)(140-20)}S_0.$$

By substituting α'' and $\bar{C}_{v_0}''$ from the foregoing table, α and $\bar{C}_{v_0}$ from Tables II and III, Part I, and S_0 from Fig. 1, we obtain for propane

$$S_0''=37.7 \quad \text{and for butane} \quad S_0''=43.4.$$

Both values are in good agreement with the experimental values shown in Fig. 2.

The same calculation was also carried out for argon where α and $\bar{C}_v$ are constant

$$S_0''=\frac{15.11(140+78.5)}{14.80(140-20)}S_0=10.65,$$

which is in good agreement with the experimental value 10.4. Another calculation was carried out for argon with a gauge wire temper-

ature of 40°C and the walls of the gauges first at 20°C and then at the temperature of liquid oxygen (−183°C). The electrical sensitivities of the bridge were 4.28 and 10.10, respectively. S_0 for the temperature difference 20°C to 40°C is taken from Fig. 1. Then $S_{0(-183 \text{ to } 40)}$ between −183°C and 40°C will be

$$S_{0(-183 \text{ to } 40)} = \frac{10.10(40+183)}{4.28(40-20)} S_0 = 18.16.$$

The experimental value is 18.14.

Knowing the accommodation coefficients and specific heats of the paraffins at various temperatures we are now able to calculate the accommodation coefficient for argon by the use of Eq. (6) Part I at the various temperatures for which sensitivity curves were taken (Fig. 1). The results are given in Fig. 3. In the temperature region between 40°C and 140°C, α for argon increases linearly within the limits of experimental error. The same figure shows accommodation coefficients of ethane, propane and butane as calculated by Eq. (5) substituting true specific heats for mean specific heats. The resulting values for the accommodation coefficient are those expected for negligibly small temperature differences between wire and wall.

A surprising relationship between the accommodation coefficients of the paraffins and that of argon is revealed by the expression:

$$\frac{\alpha_{\text{paraffin}} (C_{v_0 \text{ paraffin}} + R/2)}{\alpha_{\text{argon}} M_{\text{paraffin}}} = \text{constant}.$$

This expression is approximately constant (within a few percent) in the experimental temperature range between 40°C and 140°C. It is difficult, at present, to establish the full physical significance of this relation which permits the calculation of the accommodation coefficients of argon at various temperatures from the accommodation coefficient of the paraffins providing α_{argon} is known for *one* temperature.

Finally, sensitivity curves have been taken for ethane, ethylene and acetylene with the gauge wires at 100°C and the gauge walls at 20°C in order to verify their relationship (discussed in detail in Part I) under conditions where no break of the ethane and ethylene curves occurs as observed in case of the gauge wires being at 140°C (see Part I). The acetylene and ethylene curves fall practically together as was assumed in Part I and the ratio between the S_0 values for ethane and ethylene is identical with the ratio of the extrapolated values given in Part I.

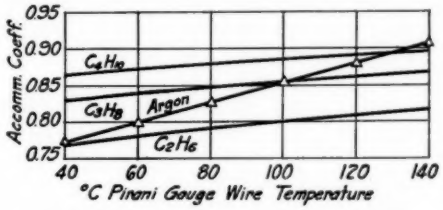

FIG. 3. The accommodation coefficients of ethane, propane, butane and argon between 40°C and 140°C on an ordinarily clean nickel surface at a pressure of some 10^{-6} mm Hg.

DISCUSSION

As has been pointed out in Part I, Eq. (3) of this paper was set up by using a value for C_{v_0} of ethane calculated from normal frequencies and an experimental value for butane from the measurements of Sage and Lacey.[4] It also was stated that an error in the latter value will produce systematic errors in all other derived values. Much confidence was placed, however, in Sage and Lacey's value for *n*-butane for reasons discussed in detail in Part I.

It is of interest, therefore, to compare our quantitative results which are partly based on Sage and Lacey's specific heat measurements of butane with results which we obtain in using propane and butane values as calculated from C−C frequencies given by Kassel[5] who estimated these frequencies by a wave mechanical treatment of nonrigid molecules, taking into account the interaction of internal rotation with vibration. He gives the following C−C frequencies:

Propane	403, 937, 1067 cm^{-1}
Butane, *cis*[6]	221, 492, 879, 1044, 1106 cm^{-1}
trans[6]	312, 385, 974, 987, 1100 cm^{-1}.

For the distribution of the C−H frequencies Kassel[7] gives:

[4] B. H. Sage and W. N. Lacey, Ind. Eng. Chem. **27**, 1484 (1935). See reference 8 in Part I.
[5] L. S. Kassel, J. Chem. Phys. **3**, 326–335 (1935).
[6] *Cis* and *trans* refer to Kassel's new type of stereoisomerism.
[7] L. S. Kassel, J. Chem. Phys. **4**, 439 (1936).

	770 cm^{-1}	1440 cm^{-1}	3000 cm^{-1}
Propane	7	7	8
Butane	10	8	10

Assuming complete free rotation about carbon-carbon bonds we calculated the mean specific heats between 20°C and 140°C and between −78.5°C and 140°C and in addition to that the true specific heat of butane at 300°C. (Table I.) If we plot these values and the respective ethane values[8] against the molecular weight, we obtain perfectly straight lines in each case. The lines for $C_{v_0(20\text{ to }140)}$ and $C_{v_0(300)}$ intersect the C_{v_0} axis at the same value, the line for $C_{v_0(-78.5\text{ to }140)}$ intersects it slightly higher. This result is in very satisfactory agreement with the assumption made in Part I that the intersection of all C_{v_0} lines with the C_{v_0} axis is constant, i.e., independent of temperature in the temperature interval between 0°C and 300°C and that according to experimental proof given in this paper this assumption holds within the limit of experimental error of ±1 percent for mean specific heat values between −78.5°C and 140°C. The lines through Kassel's values, however, intersect the C_{v_0} axis at −1.0 whereas the value found and used in this investigation is +1.80 as determined with the help of the experimental butane value of Sage and Lacey[4] which is, for the mean specific heat between 20°C and 140°C, 2.6 cal. lower than the value calculated from Kassel's theoretical frequencies. Using the C_{v_0} values calculated from Kassel's frequencies in Table I, first column, we obtain:

$$C_{v_0(20\text{ to }140)}=0.445M-1.0, \qquad (7)$$

where M is the molecular weight of the paraffin.

In substituting this value into our well-established equation for the same temperature interval:

$$(C_{v_0(20\text{ to }140)}+R/2)\alpha'=0.388M,$$

where α' is the accommodation coefficient with respect to argon, we obtain:

$$(0.445M-1.0+R/2)\alpha'=0.388M$$

or

$$\alpha'=\sim 0.388/0.445=\sim 0.87.$$

[8] The ethane values obtained from the properly assigned frequencies as given in Part I are in perfect agreement with the values obtained with Kassel's distribution of C−H frequencies: 770 cm^{-1} (4 times), 1440 cm^{-1} (6 times), and 3000 cm^{-1} (6 times); and using the well established C−C frequency of 993 cm^{-1} instead of Kassel's value 987 cm^{-1}.

TABLE I

	$C_{v_0(20\text{ to }140)}$	$C_{v_0(-78.5\text{ to }140)}$	$C_{v_0(300)}$
Propane	18.60	16.17	—
Butane	28.84	21.47	37.22

This result means that the accommodation coefficients for all paraffins are equal and below that of argon, the accommodation coefficient of which is certainly lower than unity on a brilliant nickel surface. This result is inconsistent with common knowledge and must be rejected on grounds (1) that the accommodation coefficients of the paraffins are either below unity and are then increasing with the molecular weight, or that they are equal and must be unity in this case, and (2) that it seems impossible that the higher paraffins have an accommodation coefficient lower than that of argon. Apart from the fact that the true accommodation coefficient for hydrogen reported in Part I was in excellent agreement with results of other workers, we have new experimental evidence (publication of which is forthcoming) that the true and relative accommodation coefficients for the hydrocarbons reported in Part I and in this paper are correct, which is further proof for the correctness of Sage and Lacey's value for butane on which, together with the theoretical value for ethane, the following equation (Eq. (8), Part I) was based:

$$C_{v_0(20\text{ to }140)}=0.352M+1.80,$$

as in contrast with Eq. (7) of this paper.

A good agreement is obtained, however, if the contributions of those of Kassel's frequencies which appear to be deformation (bending) frequencies of the carbon chain are omitted. With such an omission in mind we have explained satisfactorily in Part I the position of methane within our experimental results and general considerations. It is evident that any bending motion of the carbon chain is most intimately interlinked with the rotation about carbon-carbon bonds and according to E. Bauermeister and W. Weizel[9] the combined actions are neither rotations nor oscillations and must not be treated as such. It is hoped that our results will contribute to the solution of this problem. In order to gather

[9] Physik. Zeits. **37**, 169 (1936).

additional evidence, we have under way an investigation to check Sage and Lacey's value for the specific heat of butane by direct measurement.

Summary

The following is a summary of the relations found to exist for the paraffin hydrocarbons (for special consideration of methane see Part I) between the accommodation coefficient α, the specific heat at constant volume for the ideal gas state C_{v_0}, and the molecular weight M.

For constant gas and surface temperatures, the following equation holds:

$$\alpha(C_{v_0}+R/2)/M=\text{constant}, \qquad \text{(a)}$$

R being the gas constant per mole. This equation has been verified for six surface temperatures between 40°C and 140°C with a gas temperature of 20°C, and for the gas temperature of −78.5°C with a surface temperature of 140°C. In all these cases C_{v_0} was taken as the mean value between gas and surface temperature. The gas pressure was some 10^{-6} mm Hg.

An evaluation of α from Eq. (a) was possible with the help of another relation which holds for constant temperature

$$C_{v_0}=\text{constant}\cdot M+1.80 \qquad \text{(b)}$$

derived from a few reliable theoretical and experimental C_{v_0} values. The constants in both equations were found to be identical for the same temperatures. Thus:

$$\alpha=\frac{\text{constant}\cdot M}{\text{constant}\cdot M+1.80+R/2}. \qquad \text{(c)}$$

The constant may be evaluated from Eq. (b) for various temperatures or temperature intervals by using specific heat values for ethane as calculated from normal frequencies.[10] Designating the ethane values by primed symbols, we obtain:

$$\text{constant}=(C_{v_0}'-1.80)/M'.$$

This gives:

$$\alpha=\frac{(C_{v_0}'-1.80)M/M'}{(C_{v_0}'-1.80)M/M'+1.80+R/2}$$

and

$$C_{v_0}=(C_{v_0}'-1.80)M/M'+1.80.$$

Thus α and C_{v_0} may be calculated for all paraffins for any temperature by the use of specific heat values for ethane which may be calculated from normal frequencies with great accuracy. These formulae have been tested by calculating, with their help, relative heat transfers for various paraffins at various surface temperatures and with various temperature intervals between gas and surface, comprising in all the temperature range from −78.5°C to 140°C. The obtained values are in good agreement with experimental values.

Acknowledgments

As in Part I, Mr. W. H. Thurston has rendered valuable assistance in taking measurements with the molecular beam apparatus and Mr. F. Rust has prepared the pure gases.

Grateful acknowledgment is made to the directors of the Shell Development Company, especially to Dr. E. C. Williams, for their interest in this work and their permission to publish it.

[10] At present ethane is the only paraffin hydrocarbon, except methane, for which the correct assignment of normal frequencies has been possible; for details, see reference 7, Part I, p. 684.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Chemical Atomic Weights and the Relative Abundance of the Oxygen Isotopes

Nuclear disintegration experiments on the lighter elements have furnished precise atomic weights,[1] which have been confirmed in most cases by mass-spectrographic analysis. The results indicate that the whole atomic weight scale should be increased by several parts in ten thousand. These atomic weights are based on the physical scale which takes $O^{16}=16.0000$ whereas chemical atomic weights are based on the naturally occurring mixture of oxygen isotopes, $O=16.0000$. Several comparisons of chemical and physical atomic weights have been made in the past,[2] but the conversion factor is uncertain since the relative abundance of the oxygen isotopes is not known with sufficient precision. A more satisfactory conversion factor should be obtained with nonisotopic elements such as He, Be, F, Na, Al and P. However, only the chemical atomic weight of He is precise enough for this purpose. The mass of He^4 on the physical scale is 4.00395 ± 0.00007[3] and on the chemical scale, it is 4.0018 ± 0.0003.[4] An atomic weight on the physical scale may thus be converted to the chemical scale by dividing the former by 1.00054 ± 0.00008. This is considerably larger than the factor of 1.00025 previously obtained from the measured abundance of the oxygen isotopes and now used by the International Atomic Weight Committee.[5] The higher factor, however, is not unreasonable as may be seen from the following table where chemical atomic weights for several nonisotopic atoms are compared with values calculated from the physical scale by the two factors above. Definitely better agreement is noted for the higher factor except for phosphorus where the chemical atomic weight is apparently in error. The value quoted by the Atomic Weight Committee[5] is 31.02 which cannot be made to agree with the physical scale by any reasonable factor. The only other nonisotopic atoms of low atomic weight are Be and Na. For the former, there is no reliable chemical atomic weight and for the latter no precise physical atomic weight. If we take the chemical atomic weight[6] of Na as 22.9985 ± 0.0012 and convert to the physical scale, we obtain $Na^{23}=23.0009\pm0.0022$.

Comparison of the atomic weight of other light elements does not seem worthwhile because of the uncertainty in the isotopic composition. We have, however, made this comparison with both factors given above and find that no decision between the two can be made although the higher one is not excluded.

The conversion factor may also be used to compute the relative abundance of the oxygen isotopes. Since there are three of them, it was assumed that O^{18} is five times more abundant than O^{17}. The relative abundances of O^{16}, O^{17} and O^{18} are then 0.9952, 0.0008 and 0.0040, respectively. This somewhat surprising result is considerably different from the values 0.9976, 0.0004 and 0.0020 reported by the Committee on Atoms of the International Union of Chemistry.[7] We have no explanation to offer for this discrepancy but we believe that some inconsistency exists. There is no indication that the physical masses are incorrect and hence either O^{17} and O^{18} are more abundant than suspected or the chemical atomic weights of He, F and Al are considerably in error.

	Chemical Atomic Weight	Factor = 1.00025	Factor = 1.00054 ±0.00008
He	4.0018±0.0003[4]	4.0029	4.0018±0.0003
F	18.995 ±0.005[8]	19.000	18.994 ±0.002
Al	26.974 ±0.002[9]	26.984	26.976 ±0.002
P[11]	30.977 ±0.003[10]	30.976	30.968 ±0.003

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[1] For a review of the results obtained, see O. Hahn, Berichte d. deutschen chem. Gesellschaft, **70A**, 1 (1937).
[2] Birge and Menzel, Phys. Rev. **37**, 1669 (1931).
[3] Bainbridge and Jordan, Bull. Am. Phys. Soc. **11**, No. 7, Abstract 59, (1936). Atlantic City meeting.
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[6] Zintl, Zeits. f. anorg. allgem. Chemie **136**, 223 (1924).
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[9] Hoffman and Lundell, Nat. Bur. Standards J. Research **18**, 1 (1937).
[10] Richie, Proc. Roy. Soc. (London), **A128**, 551 (1930).
[11] The physical atomic weights for F and Al were taken from reference 1 and for P from Pollard and Brasefield, Phys. Rev. **50**, 890 (1936).

The Infrared Absorption Spectra of Some Polyatomic Fluorides

We have recently completed an examination of the infrared spectra of the fluorides of boron, carbon, nitrogen, and silicon. These may well be taken together since a knowledge of the four spectra is necessary before one can be certain as to the state of purity of any individual. We have been helped in the assignment of frequencies by the existence of Raman data obtained by Professor Yost for all except NF_3.

BF_3 (Anderson, Lassettre, and Yost)[1]

We find $\omega_2(||)=722$; $\omega_3(\perp)$: $B^{11}=1448$, $B^{10}=1501$ cm^{-1}. $\omega_1(||)=886$ is inactive in the infrared, and $\omega_4(\perp)$ was also located in the Raman effect at 440 cm^{-1}. Yost took ω_3 as 1038 cm^{-1}, but the isotopic doubling in the infrared leaves no doubt that it is considerably higher. K for B−F is 0.669 megadynes/cm. The molecule is plane.

NF_3

The fundamental frequencies observed are $\omega_1=908$, $\omega_2=505$ (both $||$), and $\omega_3=1004(\perp)$. The other ($\perp$) frequency ω_4 was estimated to be (420) cm^{-1}. The assignments should be taken as provisional in the absence of Raman data. The molecule is a very flat pyramid, the bond angle being 110° or more. The force constant K for N−F is low, the value 0.410 megadynes/cm corresponding to $r_e=1.45$A, instead of 1.34 from Pauling's data.

CF_4 (Yost, Lassettre, and Gross)[2]

We have succeeded in placing the active fundamental frequencies ω_3 and ω_4 at 1252 and 630 cm^{-1}, respectively. Eucken and Bertram[3] assigned ω_3 and ω_4 to two bands observed by them at 1350 and 653 cm^{-1}: the first appears to be a combination tone, and the second is too high. The Urey and Bradley force field[4] for tetrahedral molecules fits CF_4 and SiF_4 very well: K for C−F is 0.399 megadynes/cm.

SiF_4[2]

Of the active fundamentals we found $\omega_3=1022$ cm^{-1}. The other ω_4 was estimated by Yost to lie at (431) cm^{-1}. The inactive modes ω_1 and ω_2 were, respectively, found and calculated by Yost to be 800 and (285) cm^{-1}. K for Si−F is about 0.57 megadynes/cm.

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February 19, 1937.

[1] Anderson, Lassettre, Yost, J. Chem. Phys. **4**, 703 (1936).
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[3] Eucken and Bertram, Zeits. f. physik. Chemie **B31**, 361 (1936).
[4] Urey and Bradley, Phys. Rev. **38**, 1970 (1932).

The Thermal Decomposition of Ethane. A Note on the Paper by H. Sachsse

The main theme of the paper by Sachsse in the March issue under the above title is that the new value of E_4 (the activation energy of reaction (4) in the Rice-Herzfeld scheme for the decomposition of ethane) determined by us does not make as large a change in the calculated value of [H] as we say it does, our calculations being in error due to a "misunderstanding." Sachsse then recalculates [H] and shows that even with our value of E_4 the calculated values of [H] are still higher than the observed values of Sachsse by a factor of about 70.

Actually the discrepancy lies in the fact that we used the complete Rice-Herzfeld mechanism *and Rice and Herzfeld's methods of calculation* to get [H]. Sachsse, on the other hand, uses Rice and Herzfeld's set of reaction steps, but calculates the results by assuming steric factors, collision numbers, etc., which they did not use. Furthermore he puts $E_6=8$ kcal. Rice and Herzfeld do not explicitly give E_6, but from a combination of Table A and Eq. (22) of their paper it follows that they use $E_6=0$. This is the value which we used in our calculations.

On the Rice-Herzfeld mechanism $[H]=\left(\frac{k_1k_3}{2k_4k_6}\right)^{\frac{1}{2}}$. Assuming, as they do, that all bimolecular velocity constants are given by $k=10^9e^{-E/RT}$, and all unimolecular constants by $k=10^{14}e^{-E/RT}$, we obtain:

(*a*) *With $E_4=6$ kcal. as found by us, and $E_6=0$ as assumed by Rice and Herzfeld.*

$[H]=1.4\times10^{-12}$, i.e., 4 times *less* than the value found by Sachsse experimentally.

(*b*) *With $E_6=8$ kcal. as assumed by Sachsse but not by Rice and Herzfeld.*

$[H]=17\times10^{-12}$, which is only 3 times the experimental value.

(*c*) *Assuming $E_6=0$ and that the reaction occurs by a triple collision so that $a_6=0.001$.*

$[H]=46\times10^{-12}$, which is still within one power of 10 of the experimental value.

We were therefore entirely justified in saying that the value of [H] *calculated from the Rice-Herzfeld mechanism* is in almost exact agreement with Sachsse's experimental value. It follows that Sachsse's argument is with Rice and Herzfeld over the validity of their approximations, and not with our calculations. There was no "misunderstanding" on our part.

It should be emphasized that we are in complete agreement with Sachsse on the main point at issue, namely that our determination of E_4 supports the conclusion reached by Sachsse from his experiments that the Rice-Herzfeld mechanism for the decomposition of ethane is untenable. We argued that while the mechanism with the new value of E_4 now gave the approximately correct value for the hydrogen atom concentration, it could no longer be made to give the correct order or activation energy for the over-all decomposition. Sachsse argues that the predicted value of [H] is still incorrect.

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